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CHARACTERIZATION OF SULFUR RECOVERY FROM REFINERY FUEL GAS

Battelle Columbus Laboratories

Prepared for
Environmental Protection Agency

28 June 1974

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Processes for removing and recovering sulfur from refinery fuel gas are reviewed. Flowsheets, heat and material balances for Claus sulfur recovery plants and commercially available processes for sulfur removal from Claus tail gas are presented. Statistics on sulfur recovery systems in refineries are presented for 1973 and projected for 1975. The environmental impact of tail gas processes including emission reduction, liquid and solid by-products, and energy consumption is discussed.

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Prepared for

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Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

June 1974

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SUMMARY

The primary objective of Task 4 of EPA Contract 68-02-0611 was to provide an overview of available technology for treating tail gases from refinery sulfur plants. Although general information was developed pertaining to refinery desulfurization technology, emphasis was placed on estimating the environmental impact (desulfurization efficiency, utilities required, and waste streams generated) from tail-gas-treating processes.

The open technical literature was reviewed and information was collected on sulfur recovery in petroleum refineries. Inspection trips were taken to several refineries that currently are installing and/or operating tail-gas-treating processes on sulfur plants. Up-to-date nonproprietary information on commercially available tail-gas processes was then obtained from process licensors. Heat and material balances were performed and estimates were made for the required utilities, emissions, and waste streams for the Beavon, Wellman-Lord, SCOT, IFP-1500, Chiyoda, and Sulfreen processes. Insufficient information was available to permit heat- and material-balance calculations to be performed for the Cleanair Process. Estimates were then made for nationwide emissions of sulfur from domestic refineries and associated sulfur-recovery plants.

Emissions of sulfur to the atmosphere at petroleum refineries occur mainly as SO_2 in process heaters, boilers, and flares, in the tail gas from sulfur-recovery plants, and as trace amounts of H_2S which escape during routine processing operations. Virtually all sulfur recovery practiced at petroleum refineries is done by vapor-phase oxidation of H_2S in straight-through Claus plants. Domestic sulfur-recovery capacity found at refineries amounted to about 8,000 metric tons/day (MT/D) in 1973. Plants normally are operated at about two-thirds of capacity and sulfur-recovery efficiencies of 90 to 95 percent. Acid-gas-feed sources to refinery Claus plants originate mainly from sour-water strippers and amine regenerators associated with hydrocracking units, hydrotreating units, and fuel-gas-desulfurization operations. Fuel-gas desulfurization using amines and other reactive liquids as well as sulfur recovery in Claus plant is well-established technology. Both technologies are commercially available and have been practiced in the

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petroleum industry for many years

Processing of tail gases from Claus plants found at refineries would be considered emerging technology and is now only beginning to be practiced in the U.S. Approximately 964 MT/D of parent-Claus-plant capacity has been equipped with tail-gas processing on domestic refineries. These plants are now mainly in start-up and are located in the Philadelphia and Los Angeles areas. Several have been experiencing start-up difficulties. An additional 890 MT/D of parent-sulfur-plant capacity is due to be equipped with tail-gas processing units in the U.S. by 1975.

By the use of tail-gas processing, overall sulfur recovery can be increased to greater than 99 percent of the total input sulfur to Claus plants. The utilities required and waste streams generated by the operation of tail-gas processes are not inordinate. Roughly, the utilities (hence operating cost) are of the same order as those involved in the parent sulfur plant. Waste streams in processes based on aqueous-phase scrubbing usually involve either a sour-water or acid-water purge stream resulting from condensation of water vapor contained in the tail gas. Depending upon the process, this water is usually sent to either the sour-water stripper for H_2S removal or to the refinery wastewater-treatment system for neutralization. In addition, several processes, i.e., the Beavon, Cleanair, and Wellman-Lord, have purge streams containing metal salts that must be disposed of. Currently, waste streams of this latter type are being discharged to industrial sewer systems. Because of their small size, this does not appear to cause major waste disposal problems.

Nationwide sulfur emissions from refinery Claus plants were estimated to be approximately 0.136×10^6 MT/year (0.272×10^6 MT of SO_2) in 1975. In comparison with other emission sources of sulfur, refinery Claus-plant emissions appear to be quite small, i.e., the sulfur contained in refinery Claus-plant tail gases is estimated to be less than 1 percent of the 1975 unabated sulfur emission sources.

CHARACTERIZATION OF SULFUR
FROM REFINERY FUEL GAS
(Contract No. 68-02-0611, Task 4)

by

Joseph M. Genco and Samuel S. Tam

OBJECTIVE AND SCOPE

The objective of Task 4 under Contract 68-02-0611 was to assist the Emissions Standards and Engineering Division of the Environmental Protection Agency in developing standards of performance for recovery of sulfur from petroleum-refinery fuel gases. Specifically this involved providing technical information in eight areas:

(1) Defining refinery fuel gas/sour gas systems and methods of treating fuel gas to remove sulfur
(2) Estimating the fate of sulfur compounds in the fuel-gas system
(3) Defining options available for sulfur recovery
(4) Estimating the extent of sulfur recovery on current and future U.S. refineries
(5) Estimating the extent of tail-gas cleaning practiced currently at U.S. and foreign refineries
(6) Estimating the projected growth of domestic sulfur recovery for the period 1975 to 1985
(7) Estimating the environmental impact of tail-gas treating processes
(8) Assessing the environmental impact of emissions standards on sulfur recovery in the petroleum industry and putting sulfur emission from refineries into perspective with emissions from other major sources.

Although all of these areas were treated to some extent, emphasis on the program was given to tail-gas treatment from sulfur plants as defined in Item 7. The main thrust of the program was to provide an overview of available technology for treating tail gases from refinery sulfur plants. An exhaustive technical treatment of this subject was outside the scope of the present program.

METHODOLOGY

The following methodology was used in performing the study covered by this report.

(1) The open technical literature was reviewed to obtain literature on fuel-gas desulfurization in petroleum refineries. This review covered desulfurization of refinery fuel gas and sour-water stripping, vapor-phase and liquid-phase sulfur-recovery processes, and tail-gas-treating technology.

(2) Trips were made to several refineries that currently are installing and/or operating tail-gas treating equipment. Table F-1 of Appendix F lists the refineries visited, tail-gas-treatment equipment inspected, and contact dates. Both EPA and BCL personnel were involved in this part of the program.

(3) To collect up-to-date information on commercially available tail-gas-treating processes, a letter was sent to eight companies (see Appendix F, Table F-2) involved in providing tail-gas processes to the petroleum industry. Each of these companies either developed or licensed one of the leading tail gas processes. Except for the Cataban process, all are commercially available. The questions asked of each of the manufacturers are given in a sample letter included in Appendix F. Replies to this letter were received from all developers and licensors except the Societe Nationale Des Petroles d' Aquitaine, developers of the Sulfreen Process.

(4) For all tail-gas-treating processes except the Cataban and Cleanair processes, simplified heat and material balances were performed by treating the process as a "black box". Waste streams generated in the process and approximate utilities requirements were then estimated.

(5) Estimates were made for nationwide emissions of sulfur from domestic petroleum refineries and associated Claus sulfur plants.

(6) A final report was prepared.

INTRODUCTION

Individual petroleum refineries are different. Although each modern refinery is unique in design, each comprises basic unit processes employing a multitude of towers, vessels, piping, valves, tubes, exchangers, and storage tanks. Refinery operations can be classified into four basic procedures--separation, conversion, treatment, and blending.

Crude oil is initially separated into its various components or fractions, e.g., gas, gasoline, kerosene, middle distillates such as diesel fuel and fuel oil, and heavy bottoms. Since these initial fractions seldom conform to either the relative demand for each product or to the product's qualitative requirements, the less desirable fractions are subsequently converted to more salable products by splitting, uniting, or rearranging the original molecular structure. Separation and conversion products are subsequently treated for removal of undesirable components. The refined base stocks may then be blended with each other and with various additives to develop the most useful products.

Individual refineries differ widely, not only as to crude-oil capacity, but also as to the degree of processing sophistication employed. Simple refineries, often little more than "topping plants", may be confined to crude separation and limited treating (Figure 1).(1)* Intermediate refineries may add catalytic or thermal cracking, catalytic reforming,

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* References are listed on pp 99 .

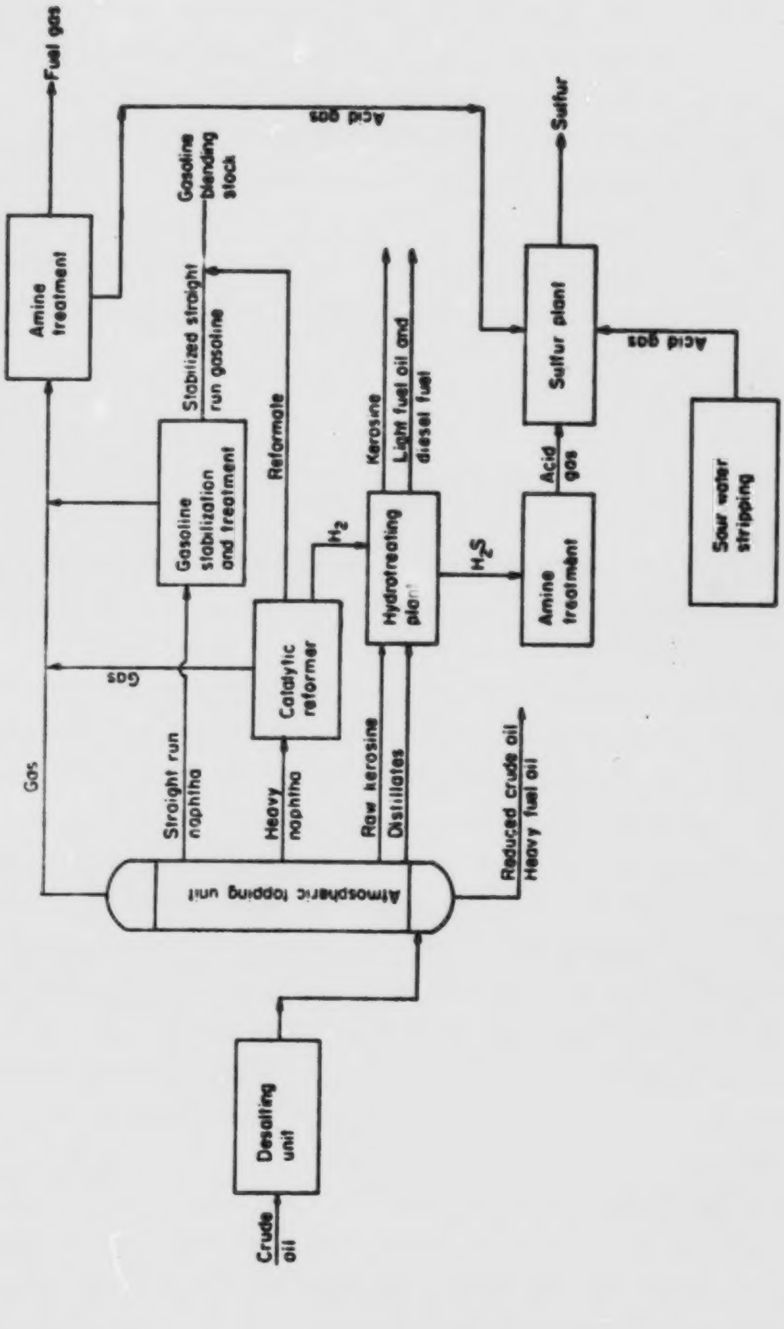
Crude oil
Desalting unit
Atmospheric topping unit
Gas
Straight run naphtha
Heavy naphtha
Raw kerosine
Distillates
Reduced crude oil
Heavy fuel oil
Gas
Catalytic reformer
Gasoline stabilization and treatment
Reformate
H2
Hydrotreating plant
H2S
Amine treatment
Acid gas
Kerosine
Light fuel oil and diesel fuel
Stabilized straight run gasoline
Gasoline blending stock
Amine treatment
Fuel gas
Acid gas
Sulfur plant
Sulfur
Acid gas
Sour water stripping

FIGURE 1. PROCESSING PLAN FOR TYPICAL MINIMUM REFINERY

distillate treating, and manufacture of such heavier products as lube oils and asphalt. Complete or "integrated" refineries are generally large in capacity, and encompass such operations as crude distillation; cracking; treating; gas processing; manufacture of lube oils, asphalts; and waxes; and gasoline-upgrading processes such as catalytic reforming, alkylation, isomerization, sweetening, and hydrogen desulfurization (Figure 2).(1)

Sulfur is considered an undesirable constituent of petroleum and occurs during processing in four general types of compounds:

(a) Hydrogen sulfide and mercaptans
(b) Elemental sulfur
(c) Carbonyl sulfide (COS) and carbon disulfide (CS_2)
(d) Neutral sulfur compounds.

Hydrogen sulfide and mercaptans (RSH) are present in all petroleum to some extent and especially prevalent in sour crude. They are also formed by thermal and catalytic decomposition of sulfur compounds during distillation, crushing, reforming, and other complex processing. Elemental sulfur per se does not occur in petroleum. When found, it is usually formed from hydrogen sulfide by oxidation owing to absorption of air during intermediate storage. Under certain economic conditions, elemental sulfur is recovered as a by-product in refinery operations. Carbonyl sulfide (COS) and carbon disulfide (CS_2) are two common forms of sulfur which are formed during petroleum processing, particularly by thermal and catalytic cracking of petroleum. Neutral sulfur compounds such as sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes, and benzonaphtho-thiophenes are originally present in crude oil and undergo numerous changes in the course of processing which alter their type, molecular weight, and distribution.

RECOVERY OF SULFUR IN PETROLEUM REFINERIES

General

The amount of sulfur emitted, mainly as SO_2, from refineries is a function of the sulfur content of the crude oil being processed, the complexity of the refinery and the refinery energy balance. Sulfur enters

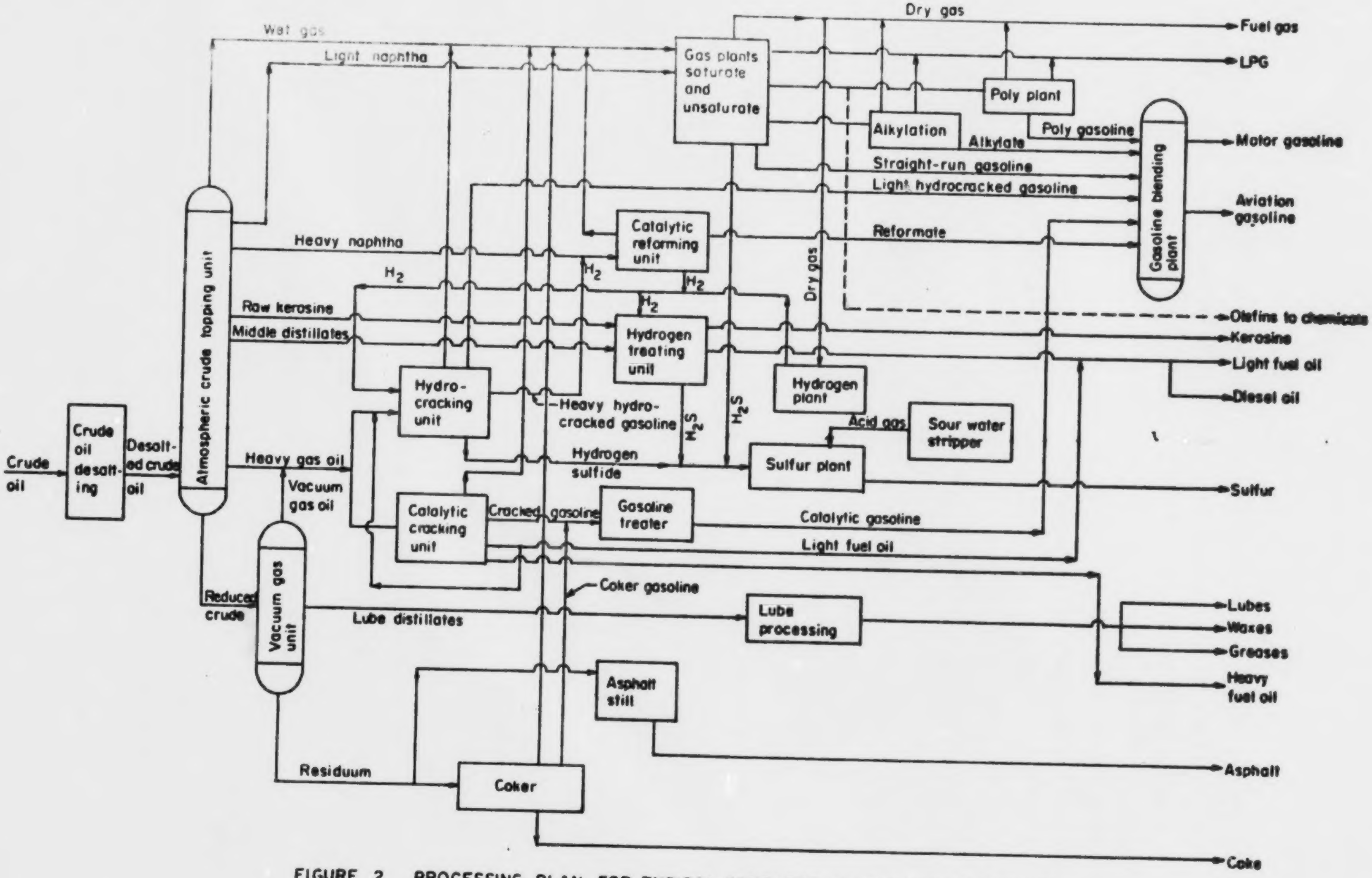
Crude oil
Crude oil desalting
Desalted crude oil
Atmospheric crude topping unit
Wet gas
Light naphtha
Heavy naphtha
Raw kerosine
Middle distillates
Heavy gas oil
Vacuum gas oil
Reduced crude
Vacuum gas unit
Lube distillates
Residuum
H_2
Hydrocracking unit
Heavy hydrocracked gasoline
Hydrogen sulfide
Catalytic cracking unit
Cracked gasoline
Coker gasoline
Coker
Asphalt still
Lube processing
Catalytic reforming unit
Hydrogen treating unit
H_2S
Gasoline treater
Catalytic gasoline
Light fuel oil
Gas plants saturate and unsaturate
Dry gas
Alkylation
Poly plant
Alkylate
Poly gasoline
Straight-run gasoline
Light hydrocracked gasoline
Reformate
Gasoline blending plant
Hydrogen plant
Sulfur plant
Acid gas
Sour water stripper
Fuel gas
LPG
Motor gasoline
Aviation gasoline
Olefins to chemicals
Kerosine
Light fuel oil
Diesel oil
Sulfur
Lubes
Waxes
Greases
Heavy fuel oil
Asphalt
Coke

FIGURE 2. PROCESSING PLAN FOR TYPICAL COMPLETE OR INTEGRATED REFINERY

the refinery in the oil, in any purchased fuel oil or gas, and in sulfuric acid purchased for use in various processes. A large part of the sulfur routinely leaves the refinery in the various products, as spent sulfuric acid shipped out for regeneration, as sulfides or sulfates in the liquid wastes, as SO_2 from process heaters and boilers and in flares, in the tail gas from the sulfur-recovery plant, and as trace amounts of H_2S that escape from the many unit operations going on in the refinery.

As shown in Figure 1, for a minimum refinery, the main sources of sulfur feed to the sulfur recovery plant are:

A. Process Gas Sources - fuel gas
   1. Atmospheric crude (topping) unit
   2. Gasoline stabilization unit
   3. Catalytic reformer
B. Hydrotreating Unit
C. Sour-Water Stripper.

In this hypothetical refinery, there are three sources of process gases; the atmospheric crude unit, the gasoline-stabilization unit, and the catalytic reformer. In each of these process gases, some H_2S is present and this is scrubbed in the amine-treatment unit before the fuel gas is used in process heaters and boilers. The acid gas or strong H_2S stream leaving the amine regenerator is sent to the sulfur plant.

A secondary source of acid-gas feed to the sulfur plant would be from the hydrotreating operations (HDS unit) used to "sweeten" the raw kerosene and other distillates from the crude column used in the manufacture of jet fuels and fuel oils. This stream would be treated in the HDS unit to remove H_2S from excess hydrogen and light ends (C_1 to C_3).

The third source of acid-gas feed to the sulfur plant would arise from the sour-water stripper. Sour water arises from many sources in the typical refinery, mainly from the atmospheric column, gasoline-stabilization unit, hydrotreater, amine-treatment units, and the sulfur plant. These sour waters are stripped of H_2S and NH_3 to produce another strong acid-gas source. This sequence of processing steps involving the recovery of sulfur within a "minimum refinery" is shown schematically in Figure 3.

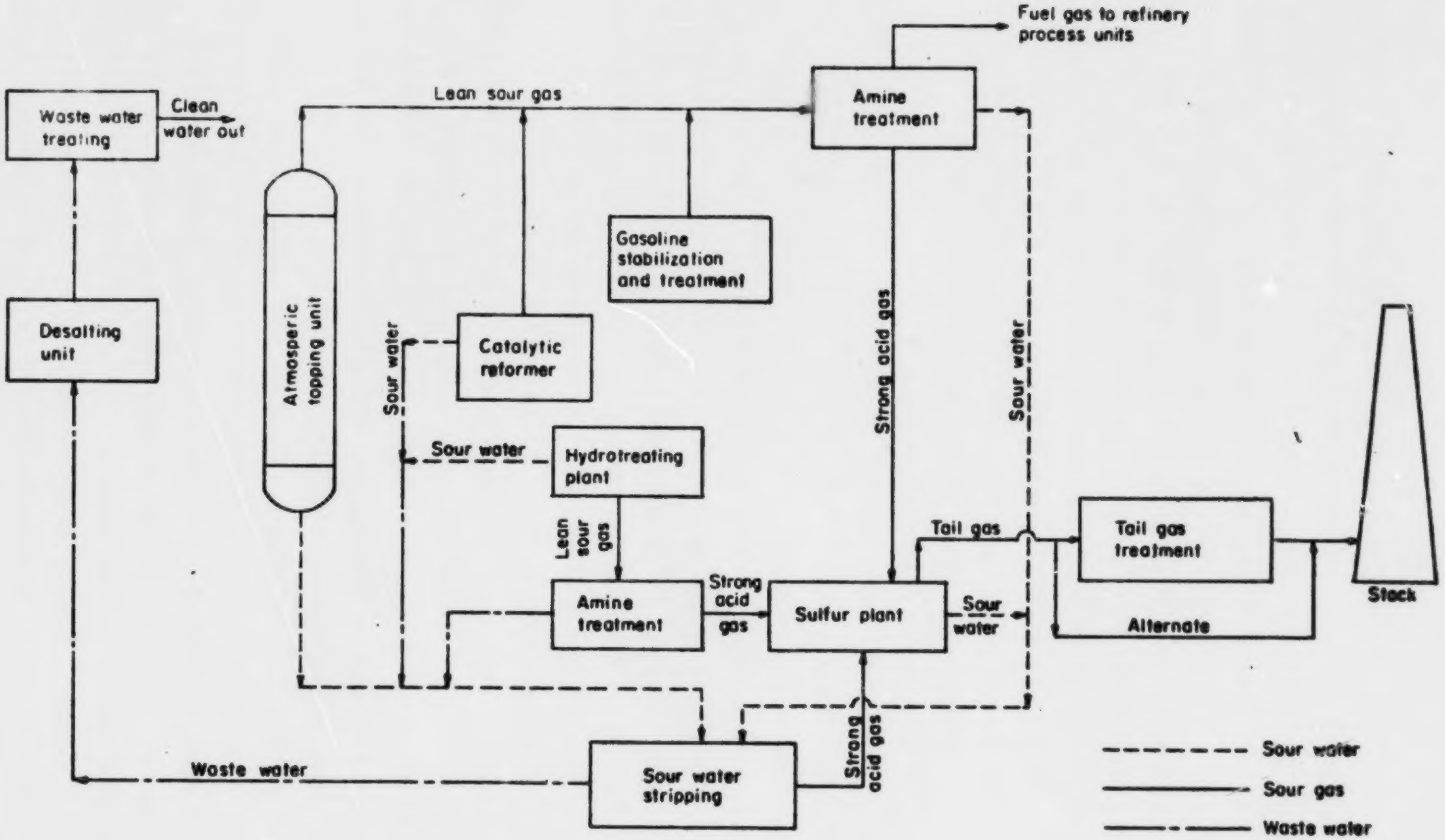
Fuel gas to refinery process units
Waste water treating
Clean water out
Lean sour gas
Amine treatment
Gasoline stabilization and treatment
Atmosperic topping unit
Desalting unit
Catalytic reformer
Sour water
Strong acid gas
Sour water
Sour water
Hydrotreating plant
Lean sour gas
Tail gas
Tail gas treatment
Stack
Amine treatment
Strong acid gas
Sulfur plant
Sour water
Alternate
Waste water
Sour water stripping
Strong acid gas
Sour water
Sour gas
Waste water

FIGURE 3. SCHEMATIC FLOW DIAGRAM SHOWING SOUR WATER/SOUR GAS STREAMS (TYPICAL MINIMUM REFINERY)

For the complex integrated refinery shown in Figure 2, acid gas from four sources would be fed to the sulfur plant:

A. Process Gas Sources - fuel gas
   1. Atmospheric crude unit
   2. Hydrocracking unit
   3. Catalytic cracking unit
   4. Coker
   5. Reformer

B. Hydrocracking Unit

C. Hydrotreating Unit

D. Sour-Water Stripper.

A schematic diagram (see Figure 4) showing the sour-gas and sour-water streams for an integrated refinery is more complex but quite similar to that shown in Figure 3. The refinery would have three amine-treatment units (one each for the fuel-gas system, the hydrocracker, and the hydrotreater) as well as a sour-water stripper.

The technology available for recovery of sulfur in petroleum refineries can be divided into four categories.

(1) Fuel-gas-treatment processes
(2) Sour-water stripping
(3) Acid-gas treatment - i.e., Claus-plant technology and alternative methods of sulfur recovery
(4) Tail-gas-treating processes.

Pertinent technology on fuel-gas-treating processes, acid-gas treating, and tail-gas-treating processes is summarized in Table 1.

Processes for the Removal of Hydrogen Sulfide from Refinery Process-Gas Streams

Many regenerable methods are available for the removal of hydrogen sulfide from refinery process-gas streams. Only the following more important processes are discussed here (see Table 1):

Girbotol Process (Girdler)
Adip Process (Shell)
Phosphate Process (Shell)
Econoamine Process (Fluor).

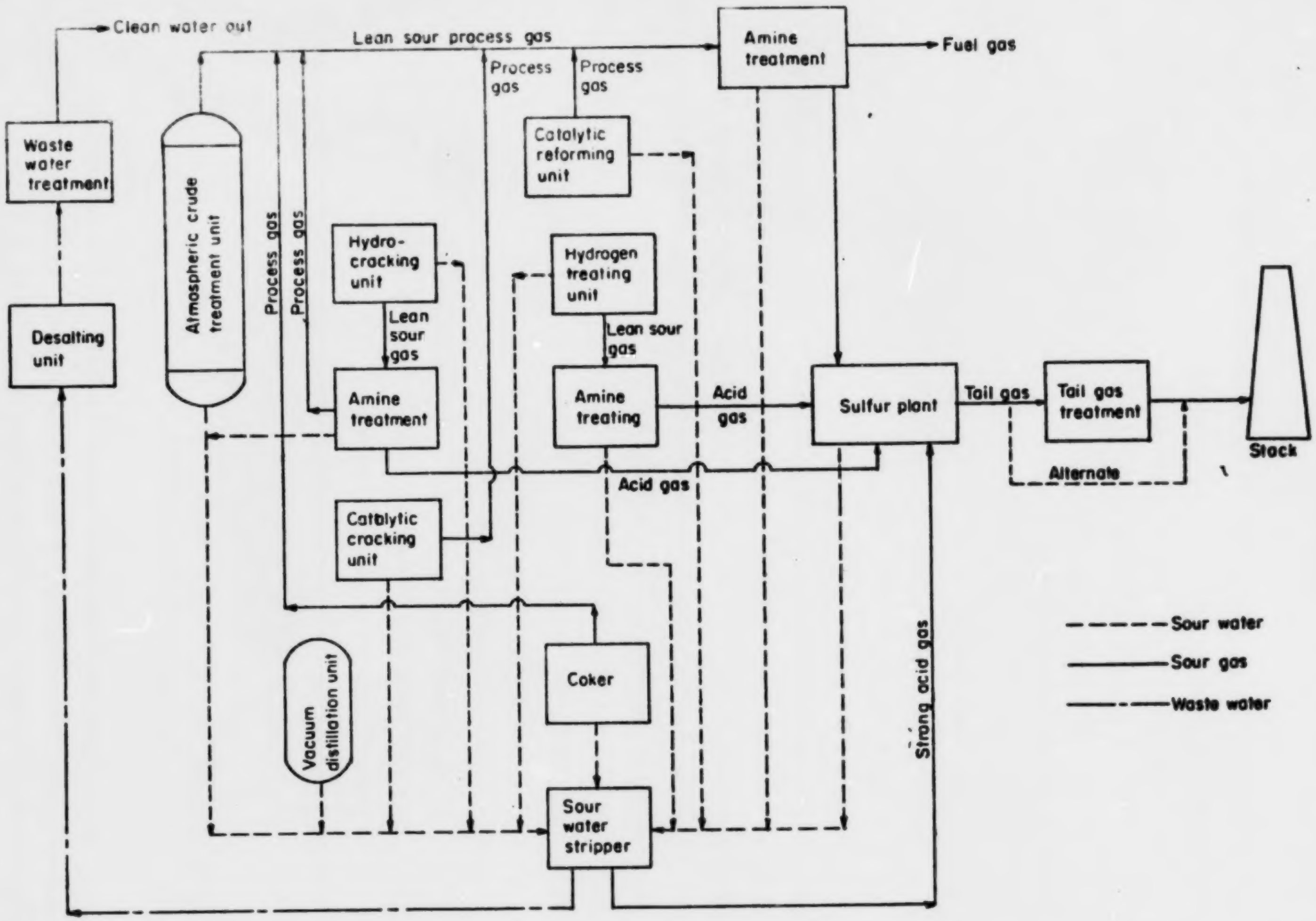
Clean water out
Lean sour process gas
Amine treatment
Fuel gas
Process gas
Process gas
Waste water treatment
Atmospheric crude treatment unit
Process gas
Process gas
Catalytic reforming unit
Hydro-cracking unit
Hydrogen treating unit
Lean sour gas
Lean sour gas
Desalting unit
Amine treatment
Amine treating
Acid gas
Sulfur plant
Tail gas
Tail gas treatment
Stack
Alternate
Acid gas
Catalytic cracking unit
Vacuum distillation unit
Coker
Sour water stripper
Strong acid gas
Sour water
Sour gas
Waste water

FIGURE 4. SCHEMATIC FLOW DIAGRAM SHOWING SOUR WATER/SOUR GAS STREAMS (TYPICAL INTEGRATED REFINERY)

TABLE 1. SUMMARY OF UNIT PROCESSES IN REFINERY FUEL-GAS DESULFURIZING

Process	Basis	Process Temp, C	Process Pressure, atm	Regeneration	Product Form
Fuel-Gas Treatment	**Liquid Chemical Absorption**				
Adip Process (Shell)	**Aqueous amines, di-isopropanol**	30- 55	1-70	(a)	H_2S
Girbotol Process (Girdler)					
Monoethanolamine (MEA)	15-20% aqueous solution	30- 55	1-70	(a)	H_2S
Diethanolamine (DEA)	15-20% aqueous solution	30- 55	1-70	(a)	
Triethanolamine (TEA)	15-20% aqueous solution	30- 55	1-70	(a)	H_2S
Econoamine Process (Fluor)	Alkanolamine (DGA)	30- 55	1-70	(a)	H_2S
Shell Phosphate Process (Shell)	Aqueous K_3PO_4	30- 55	1-70	(a)	H_2S
Acid-Gas Treatment	**Vapor-Phase Oxidation**				
Claus Process	Gas-phase catalytic oxidation	200-260	1-2	none	S
	Liquid-Phase Oxidation				
Giammarco-Vetrocoke - H_2S (Powergas Corp.)	Solution oxidation of H_2S absorbed as thioarsenite with arsenate/arsenite air regenerated redox couple as oxygen carrier	30- 55 30- 55	1-70 1-70	Air blowing Air blowing	S S
Stretford	Solution oxidation of H_2S (absorbed as bisulfide) by two-stage redox reaction involving vanadate and anthraquinone disulfonic acid as the oxygen carriers	30 - 55 30- 55	1-70 1-70	Air blowing Air blowing	S S
Tail-Gas Treatment	**Liquid-Chemical Absorption**				
Wellman Lord	Aqueous $NaSO_3/NaHSO_3$ absorption	45- 55	$1^{(b)}$	Thermal regeneration	$SO_2^{(c)}$
Beavon	Cat. hydrogenation to reduce COS, SO_2, and CS_2 to H_2S for feed to Stretford	$30\text{-}\ 55^{(d)}$	$1^{(b)}$	Air blowing	S
Cleanair	H_2S-rich tail gas water cooled to continue Claus reaction and hydrolyze COS and CS_2 to H_2S; final H_2S sent to Stretford	45- 55	$1^{(b)}$	Air blowing	S
SCOT	Cat. hydrogenation to reduce COS, SO_2, and CS_2 to H_2S for feed to an alkanolamine absorption unit	$30\text{-}\ 55^{(e)}$	$1^{(b)}$	(a)	$H_2S^{(c)}$
IFP	Claus redox reaction in solution with or without added catalyst	125-150	$1^{(b)}$	none	S
Chiyoda	Absorption of SO_2 in dilute H_2SO_4 containing $Fe_2(SO_4)_3$ catalyst	45- 55	$1^{(b)}$	(f)	$CaSO_4 \cdot 2H_2O$
	Vapor-Phase Oxidation				
Sulfreen	Catalytic use of activated carbon for high efficiency Claus redox reaction to yield sulfur	125-150	$1^{(b)}$	Hot nitrogen	S

(a) Regenerate rich solution in a reboiled stripper column.
(b) Process operated near atmospheric pressure with sufficient pressure to overcome the pressure drop in the system.
(c) Recycle off gas to the Claus process.
(d) Beavon process has a catalytic hydrogenation (reduction step) that is operated at about 315+ C.
(e) SCOT process has a catalytic hydrogenation step that is operated at about 315+ C.
(f) Sulfuric acid neutralized with limestone.

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Schematic flow diagrams for all of these processes are presented in Appendix A.

Girbotol Process. Hydrogen sulfide and carbon dioxide readily combine with aqueous solutions of certain aliphatic amines at temperatures usually close to ambient, and may be driven off from the fat solutions by heating to about 100 C. The reactions with hydrogen sulfide and carbon dioxide are essentially:

$$RNH_2 + H_2S \rightleftarrows RNH_3HS$$

$$RNH_2 + CO_2 + H_2O \rightleftarrows RNH_3HCO_3 \quad .$$

The above reaction with H_2S forms the basis of the well-known Girbotol process$^{(2-4)}$ (see Figure A-1). The amines normally used are the mono-, di-, and triethanolamines. Currently, the material most commonly used is diethanolamine. Monoethanolamine has a higher absorptive power for hydrogen sulfide and carbon dioxide per volume of treating solution, but has the disadvantage that any carbonyl sulfide present in the gas combines irreversibly with it. The triethanolamines have poorer absorptive powers but are more selective, removing carbon dioxide only to a relatively small extent. The treating solution contains from 15 to 20 weight percent of the amine.

Conventional equipment is used, generally a bubble-cap tower when refinery gases are to be treated, together with a bubble-cap tower for regeneration. Treatment takes place at line pressure but care must be exercised to see that the treating temperature is 5 to 10 C above the hydrocarbon dew-point temperature of the gas to ensure that no hydrocarbon liquid condenses out in the plant.

The Girbotol process is perhaps the most widely used method for the regenerative removal of hydrogen sulfide from refinery gases. However, its use is not confined to refineries. The simple and usually troublefree nature of the process renders it an excellent treatment tool for natural gas and LPG in oil fields, where the plants give excellent service with a minimum of attention. Utility requirements are quite low and the plants are quite flexible, being readily capable of yielding products containing only very small amounts of hydrogen sulfide. However, where the hydrogen sulfide content of the effluent gas must be reduced to less than 1 or 2 ppm or lower, it is usually more economic to follow treatment in the Girbotol plant with a nonregenerative soda wash rather than to incur the very high solvent circulation rate and very complete regeneration needed if the Girbotol plant alone has to meet requirements.

Adip Process. The Adip process(5) (Figure A-2) is very similar to the Girbotol process and numerous units are in operation throughout the world. The process is based on regenerative absorption of solvent amines in equilibrium reaction with acidic gases. H_2S-containing feed is contacted countercurrently with Adip (aqueous alkaline di-isopropanol amine) solution in an absorption or extraction column. Regenerated solution is introduced into the head of the absorption column at a normal or slightly higher temperature and leaves at the bottom of the column. Rich solution exchanges heat with the regenerated solution and is fed to the regenerator. Acid gases are stripped in the regenerator column, which is equipped with a steam reboiler. Cooled regenerated solution is recycled into the absorber.

Acid gases removed from solution in the regenerator are cooled with air and water, thus condensing the water vapor which is refluxed into the tower. All absorbed H_2S is concentrated in the acid gas stream.

Steam consumption in the process is reduced when removing H_2S from gases under pressure because higher absorption temperatures are possible. H_2S in the product can be reduced to meet stringent specifications thus making after-treatment unnecessary. Wide flexibility is possible in setting operating conditions. The absorber conditions are set by the pressure of the feed stream and range from near atmospheric pressure to about 70 atmospheres of pressure. The regenerator normally operates at slightly above atmospheric pressure such that low-pressure (about 5 atmospheres) steam is suitable for reboiler heat.

Solvent circulation rates are dependent on the total gas feed rate and concentration of acidic gases in the feed.

Shell Phosphate Process. The Shell phosphate process[(6)] utilizes an aqueous solution of tri-potassium phosphate for the removal of hydrogen sulfide from gaseous and liquid streams according to the following reaction:

$$K_3PO_4 + H_2S \rightleftarrows K_2HPO_4 + KHS \quad .$$

A flow diagram for the phosphate process is presented in Figure A-2. Absorption takes place at ambient temperature, usually in a bubble-cap tower. The hydrogen sulfide is recovered from the fat solution by reboiling in a bubble-cap tower. Regeneration is also assisted by the fact that absorption usually takes place at a considerable pressure (10 to 70 atmospheres), whereas the pressure in the regenerator is only slightly above atmospheric. It can be noted in the flowsheet that the usage of steam for reboil heat has been minimized by designing the regenerator to produce both a "very lean" solution and a "lean" solution. The "very lean" solution is fed to the top of the absorber to ensure that the treated stream is contacted last with the liquor of highest power for the removal of hydrogen sulfide, while the "lean" solution enters lower down the absorber, where it effects the removal of the bulk of the hydrogen sulfide. This splitting of the lean-solution flow is normally used for gas treating where a product of very low hydrogen sulfide content is required; for treating refinery gases, the conventional single lean-solution flow is normally adequate.

Since tri-potassium phosphate is a stable inorganic salt that does not decompose or vaporize under treating conditions, it does not contaminate the hydrocarbons in any way. Furthermore, solution loss is negligible. There are no corrosion problems, and mild steel is, therefore, a satisfactory material of construction.

An important point to note is that there is little concomitant removal of carbon dioxide. This factor may often weigh heavily in favor of the process and more than counterbalance the rather high steam consumption since frequently the removal of carbon dioxide is either unnecessary or undesirable. Furthermore, as the recovered hydrogen sulfide contains little carbon dioxide and hydrocarbons, it is eminently suitable for the manufacture of elemental sulfur in a Claus plant.

Econoamine Process (DGA). Frequently, a gas must be dried as well as purified of hydrogen sulfide. This is true of natural gas for domestic distribution, where water must be removed in order to prevent condensation in the line and the formation of solid hydrates at low temperatures. The two operations may be combined in the glycol-amine process using a solvent of di- or triethylene glycol plus mono- or diethanolamine together with some water. A good example of this type of process is the Econoamine process(7) which uses an aqueous solution of the primary alkanolamine ($OCH_2H_4OC_2H_4NH_2$) having the trade name diglycolamine (see Figure A-4). The operation of the Econoamine process is very similar to the Girbotol and Adip processes.

Sour-Water Stripping as a Source of Refinery Sulfur

In petroleum refining, various processing operations produce wastewater solutions, principally condensates containing sulfides. These sulfides are generally present as hydrogen sulfide in the presence of ammonia, mercaptans, phenolics, and possibly small amounts of water-soluble organic acids, nitrogen bases, and cyanides. These wastewaters are generally referred to as "foul waters" or "sour waters". The principal sources of foul waters are condensates from accumulators, reflux drums and knockout pots in catalytic reformers, cracking, hydrocracking, coking, and crude distillation. Table 2 presents several typical sources of sour condensate.(8)

The amount of H_2S in sour condensate is related to the H_2S partial pressure in the vapor phase at the condensate source. If the source drum contained only H_2S, hydrocarbon vapor, and water, equilibrium H_2S-H_2O conditions would be attained. However, this is rarely the case. Almost invariably there is also a hydrocarbon liquid phase present, and the hydrocarbon liquid forms a layer between the vapor phase and the sour condensate. Thus, it is doubtful that true H_2S-H_2O equilibrium is reached between the vapor phase H_2S and the sour condensate. Also, in most cases, ammonia is present because of one or both of the following reasons:

TABLE 2. TYPICAL SOUR CONDENSATE SOURCES(8)

Process	Effluent Condensate Source	Original Steam Source
Crude oil distillation	Distillation reflux drum	Stripping steam, water in crude oil
Petroleum coking (Thermal cracking)	Distillation reflux drum	Stripping steam, coke drum steam, heater injection steam
Petroleum visbreaking (Thermal cracking)	Distillation reflux drum	Stripping steam, heater injection steam
Vacuum distillation	Distillation overhead	Stripping or diluent steam, ejector motive steam
Petroleum catalytic cracking	Distillation reflux drum	Stripping steam, catalyst stripping steam
Catalytic hydrodesulfurization	Product stripper reflux drum	Stripping steam
Catalytic reforming	Product stripper reflux drum	Stripping steam
Petrochemical processes (Thermal cracking of hydrocarbons)	Quench systems and/or distillation reflux drum	Reaction diluent steam

(a) Ammonia is usually injected into fractionator overhead systems to neutralize the H_2S and to avoid the corrosion caused by acidic H_2S in the sour condensate.

(b) Nitrogen in the process feedstock is hydrogenated and forms free ammonia.

Aqueous-phase concentration data for 13 different sour waters are presented in Table 3.(8)

Essentially, sour waters and sour condensates are aqueous solutions of NH_3 and H_2S which may contain as much as 10,000 ppm of H_2S. The molar ratio of NH_3 to H_2S varies from about 1.0 to about 2.0, with an average of 1.5. The alkalinity ranges from 7.8 to 9.3 pH. The NH_3 and H_2S are present in solution in equilibrium with NH_4^+ ion and SH^- ion. The overall equilibrium can be depicted as follows:

$$NH_3(g) \rightleftarrows NH_3(\ell)$$

$$H_2S(g) \rightleftarrows H_2S(\ell)$$

$$NH_3(\ell) + H_2S(\ell) \rightleftarrows NH_4^+ + SH^- \quad .$$

Roughly speaking, the free H_2S in solution would be proportional to the partial pressure of H_2S in the gas phase, in the absence of a hydrocarbon layer. Most refineries and petrochemical plants include facilities for stripping H_2S and, in some cases, NH_3 from their sour-water streams. In those cases where sulfur recovery is practiced, the off gas from the stripper is routed to the sulfur recovery plant. When sulfur recovery is not practiced, the sour off-gas stream is usually incinerated. Sour-water strippers are normally considered part of the wastewater-treatment system.

Many different types of sour-water strippers and methods of stripping are used commercially, but most of them involve the downward flow of sour water through a tray or packed tower while an ascending flow of stripping steam, fuel gas, or flue gas removes the H_2S and, in some cases, the NH_3. The operating conditions vary from 1 to 4.4 atmospheres and from 35 to 130 C. The sour water may or may not be acidified with mineral acid (H_2SO_4 or HCl) prior to stripping.

TABLE 3. API DATA ON SOUR WATERS(8)

H_2S		NH_3		Phenols		pH	
Range	Avg	Range	Avg	Range	Avg	Range	Avg
275-500	390	100-700	135	--	--	7.5-8.0	7.75
--	1,500	--	1,000	--	100	--	8.00
--	5,000	--	5,000	--	--	--	--
--	7,200	--	5,000	--	--	--	--
--	4,800	--	3,600	--	--	--	8.30
3,000-11,000	7,000	3,500-6,000	4,750	--	--	--	--
7,500-9,000	8,250	6,100-7,000	6,550	700-1,000	900	8.4-8.8	8.60
--	4,000	--	3,000	--	800	--	8.70
1,600-2,500	2,050	2,000-2,300	2,150	--	--	8.5-9.0	8.75
--	8,000	--	5,000	--	--	--	8.50
--	1,876	--	1,480	--	102	9.0-9.5	9.25
--	1,020	--	748	--	220	--	8.50
--	3,000	--	2,400	--	--	--	8.40

Notes: 1. The H_2S partial pressure in source drums is estimated to be probably 0.007 to 0.3 atmosphere.

2. H_2S, NH_3, and phenol concentrations are in ppm by weight.

H_2S is much easier to remove than is NH_3. In pure water at 38 C, for example, Henry's Law coefficient for NH_3 is 5.6×10^5 ppm/atm, while that for H_2S is 2.7×10^3 ppm/atm. To remove efficiently about 90 percent of the NH_3, a temperature of 110 C or higher is usually employed. For the same stripping gas rate, 90 percent of the H_2S could be removed at lower temperatures.

The use of mineral acids to acidify the sour water, prior to stripping, fixes the NH_3 as NH_4Cl or $(NH_4)_2SO_4$. These are salts of strong acids and a weak base, so the free NH_3 formed by hydrolysis is practically nil; hence the NH_3 is fixed in solution. This releases the H_2S and 90 percent or more of the H_2S can be removed at 38 C. The use of flue gas as a stripping medium introduces CO_2 into the system, and this is not done when H_2S is to be recovered in a sulfur plant. Also, fuel gas, or any inert gas, can be used to strip H_2S from sour water. However, stripping H_2S with fuel gas has the disadvantage of contaminating the fuel gas with both H_2S and water. Again this is not done when H_2S is to be recovered.

The majority of installed sour-water strippers employ steam as both a heating medium and a stripping gas. Some of these are provided with overhead condensers to remove the stripping steam from the overhead H_2S and NH_3. The condensed steam is recycled or refluxed to the stripper. Table 4 presents some available data on steam strippers(8) and their performance. An example of a sour-water stripper in which both H_2S and NH_3 are recovered (no acidification) is shown in Figure B-1. This figure shows a stripper designed to handle sour waters and condensates from several refinery processes (thermal cracker, fluid coker, and gas plant) in one unit.(9) Figure B-2 presents a typical design for stripping H_2S from highly ammonical foul waters in which NH_3 is not recovered (mineral acid fixation).(9) Both processes employ steam as the stripping medium. A block diagram for the recovery of NH_3 as well as H_2S is shown in Figure B-3.(10) These components are separated, respectively, into a high-purity NH_3 stream suitable for sale or use within the refinery, a H_2S stream suitable for conversion into sulfuric acid or sulfur, and a clean-water stream suitable for reuse in process plants or for direct discharge following aeration to restore oxygen content if necessary.

TABLE 4. PERFORMANCE DATA FOR SOUR-WATER STRIPPERS(8)

	Stripping Medium, scf/gal(a)	Percent Removal		Temperature at Tower Bottoms, C
		H_2S	NH_3	
Steam strippers				
Without Acidifying	60-239	96-100	69-95(f)	110-132
With Acidifying	30-45	97-100	0	110-121
Fuel-gas strippers				
With Steam(c)	95	88-98	77-90	113+
With Steam(d)	89	99	8	60
Fuel-gas stripper				
With Acidifying(e)	56	98	0	21-38

(a) Standard liters of stripping medium per liter of total tower feed including reflux.

(b) Excluding one unexplainably high value.

(c) Based on data from one tower. Stripping medium was 90 volume percent steam-10 volume percent flue gas.

(d) Based on data from one tower.

(e) Based on data from one tower. NH_3 removal assumed as 0 percent because of acidifying.

(f) Range would be 86 to 95 percent if one low value were excluded.

CONVERSION OF RECOVERED H_2S INTO ELEMENTAL SULFUR

In refinery technology, two general categories of processes are available for recovery of elemental sulfur from H_2S. Both classes of processes involve the oxidation of H_2S to elemental sulfur utilizing the overall simplified reaction

$$H_2S + 1/2\ O_2 \rightarrow S + H_2O.$$

The mechanism by which the above reaction occurs is greatly different in the two cases and involves vapor-phase catalytic oxidation in one case (classical Claus-plant technology) and liquid-phase oxidation in the other. The essence of each method is described in the following paragraphs.

Vapor-Phase Oxidation of H_2S to Elemental Sulfur--Claus-Process Technology

The Claus process has been proven effective in converting hydrogen sulfide to elemental sulfur. The efficiency varies from 90 to 99 percent, depending on the concentration of hydrogen sulfide in the sour gas and the number of stages. A typical Claus plant will recover about 94 percent of the sulfur feed. Depending upon the concentration of hydrogen sulfide in the sour gas, there are four main types of Claus processes: (1) straight through, (2) split flow, (3) sulfur recycle, and (4) direct oxidation. Since the advent of economical fuel-gas-treatment and sour-water-treatment processes from which enriched streams of hydrogen sulfide are obtained, the straight-through Claus process has been used almost exclusively in the petroleum refinery industry.

Claus plants are widely used for recovering by-product sulfur from petroleum. A plant-by-plant listing of refinery sulfur capacity is given in Table 5 and summarized state by state in Table 6.(11) A typical two-stage packaged Claus plant found in refineries for the purpose of sulfur recovery is shown in Figure C-1. The basic exothermic reactions for this process are:

TABLE 5. LISTING OF REFINERY CLAUS SULFUR PLANT CAPACITY IN THE UNITED STATES(11)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,(a) metric tons*
ALASKA		
Energy Co. Alaska		
Fairbanks, North Star	1972	9
ARKANSAS		
Monsanto Co.		
Eldorado, Union	Before 1961	25
CALIFORNIA		
Monsanto Co.		
Avon	Before 1967	132
Union Oil Co. of California		
Santa Maria, Santa Barbara	1954	55
Allied Chemical Corp.		
Richmond, Contra Costa	Before 1962	100
Expansion	1968	+100
Humble Oil & Refining Co.		
Benicia, Solano	1969	270, two trains
Shell Oil Co.		
Martinez, Contra Costa	1966	100
Union Oil Co. of California		
San Francisco, San Mateo	1955	70
Expansion	1971	+75
Allied Chemical Corp.		
El Segundo, Los Angeles	1959	175 standby
Expansion	1964	+100
Atlantic Richfield Co.		
Wilmington, Los Angeles	1967	65
Collier Carbon and Chemical Corp.		
Los Angeles, Los Angeles	Before 1972	Not reported
Continental Oil Co.		
Paramount, Los Angeles	1966	9
Fletcher Oil & Refining Co.		
Wilmington, Los Angeles	Before 1962	7 standby
Golden Eagle Refining Co. Inc.		
Torrance, Los Angeles	1959	4 standby
Gulf Oil Corp.		
Santa Fe Springs, Los Angeles	Before 1961	8
Expansion	Before 1962	9
Expansion	1964	13

TABLE 5. (Continued)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,[(a)] metric tons*
CALIFORNIA		
Mobil Oil Corp.		
Torrance, Los Angeles	1967	85
Expansion	1973	Not reported
Powerine Oil Co.		
Santa Fe Springs,Los Angeles	1957	20
Standard Oil Company of California		
El Segundo, Los Angeles	1972	450
Stauffer Chemical Co.		
Wilmington, Los Angeles	Before 1962	100
Expansion	Before 1962	+20
Expansion	1962	+140
Expansion	1964	+8
Expansion	1967	+132
Expansion	Before 1972	+50
Texaco, Inc.		
Los Angeles, Los Angeles	Before 1962	50
Union Oil Co. of California		
Wilmington, Los Angeles	1952	49
Expansion	1962	+100
Expansion	1973	+200
COLORADO		
Continental Oil Co.		
Denver, Adams	1968	18
DELAWARE		
Getty Oil Co.		
Delaware City, New Castle	1956	375
Stauffer Chemical Co.		
Delaware City, New Castle	Before 1962	260
Expansion	Before 1972	+140
HAWAII		
Dillingham Petroleum Corp.		
Barbers Point, Honolulu	1972	Not reported
ILLINOIS		
Anilin Company of Illinois		
Wood River, Madison	1960	150
Marathon Oil Co.		
Robinson, Crawford	1970	40

TABLE 5. (Continued)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,(a) metric tons*
Mobil Oil Corp.		
Joliet, Will	1972	300
Union Oil Co. of California		
Lemont, Cook	Before 1961	20
Expansion	1964	+34
Expansion	1971	+25
INDIANA		
American Oil Co.		
Whiting, Lake	1952	64
Expansion	1964	+40
Expansion	1972	+43
Expansion	1972	+132
Atlantic Richfield Co.		
East Chicago Lake	1971	85
Cities Service Oil Co.		
East Chicago, Lake	1972	50
KANSAS		
Farmland Industries, Inc.		
Coffeyville, Montgomery	1968	6
Phillips Petroleum Co.		
Kansas City	1968	38
LOUISIANA		
Cities Service Oil Co.		
Lake Charles, Calcasieu	1972	100
Gulf Oil Corp.		
Belle Chasse, Plaquemines	1972	40
Humble Oil & Refining Co.		
Baton Rouge	1967	10
Expansion	1972	+300
Stauffer Chemical Co.		
Baton Rouge	1950	30
Shell Oil Co.		
Norco, St. Charles	1965	40
Texaco, Inc.		
Paradis, St. Charles	1966	50
MICHIGAN		
Leonard Refineries, Inc.		
Alma, Gratiot	1956	12

TABLE 5. (Continued)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,[a] metric tons*
Marathon Oil Co.		
Detroit	Before 1961	27
Expansion	1962	+8
Expansion	1968	+34
Mobil Oil Corp.		
Woodhaven, Trenton	1962	8
MINNESOTA		
Great Northern Oil Co.		
Pine Bend	1955	60
Expansion	1963	+70
North Western Refining Co.		
St. Paul Park, Washington	1968	40
MISSISSIPPI		
Gulf Oil Corp.		
Purvis, Lamar	Before 1961	30
Chevron Oil Co.		
Pascagoula, Jackson	1972	Not reported
MISSOURI		
American Oil Co.		
Sugar Creek, Jackson	1971	80
MONTANA		
Farmers Union Central Exchange		
Laurel, Yellowstone	1969	28
Montana Sulfur & Chemical Co.		
East Billings, Yellowstone	Before 1972	120 standby
Montana Sulfur & Chemical Co.		
Billings, Yellowstone	1956	40
Expansion	1964	+45
NEW JERSEY		
Allied Chemical Corp.		
Elizabeth, Union	1958	30 standby
American Cyanamid Co.		
Bound Brook, Somerset	1967	12
Expansion	1972	Not reported
Anilin Company of New Jersey		
Perth Amboy, Middlesex	1957	35
Expansion	1962	+15

TABLE 5. (Continued)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,[a] metric tons*
Amerada Hess Corp.		
Port Reading, Middlesex	Before 1967	40
Humble Oil & Refining Co.		
Linden, Union	1970	300, two trains
Freeport Sulfur Co.		
Westville, Camden	Before 1961	30
Mobil Oil Corp.		
Paulsboro, Camden	Before 1961	95
Expansion	1972	+90
NEW MEXICO		
El Paso Natural Gas Co.		
Eunice, Lea	Before 1961	30
NEW YORK		
Ashland Oil, Inc.		
Buffalo	1969	50
NORTH DAKOTA		
Signal Oil & Gas		
Tioga, Williams	1953	50
Expansion	1963	+23 standby
Expansion	1967	+150
OHIO		
Ashland Oil, Inc.		
Canton, Stark	1970	50
Sun Oil Co.		
Toledo	1958	12
Expansion	1972	+27
PENNSYLVANIA		
Atlantic Richfield Co.		
Marcus Hook, Delaware	Before 1961	20
Expansion	1962	+32
Atlantic Richfield Co.		
Philadelphia, Philadelphia	1964	38
Expansion	1971	+35
BP Oil Corp.		
Marcus Hook, Delaware	Before 1972	52
Gulf Oil Corp.		
Philadelphia, Philadelphia	Before 1961	135
Sun Oil Co.		
Marcus Hook, Delaware	1955	30

TABLE 5. (Continued)

State/Company/City, County	Year Sulfur Production Started	Daily Sulfur Capacity,[(a)] metric tons*
TEXAS		
Sulpetro Corp.		
Big Spring, Howard	1966	10
Diamond Shamrock Corp.		
Sunray, Moore	1951	30
Phillips Petroleum Co.		
Borger, Hutchinson	1968	33
Coastal States Petrochemical Co.		
Corpus Christi, Nueces	1972	85
Phillips Petroleum Co.		
Sweeny, Brazoria	1967	25
Atlantic Richfield Co.		
Houston, Harris	1960	30
Expansion	1970	Not reported
Signal Oil & Gas Co.		
Houston, Harris	1963	40
Expansion	1967	10
Shell Oil Co.		
Deer Park, Harris	Before 1962	50
Expansion	1966	+50
Expansion	1970	+300, two trains
Stauffer Chemical Co.		
Baytown, Harris	1953	70
Expansion	1962	+121
Atlantic Richfield Co.		
Port Arthur, Jefferson	1961	38
Expansion	1967	+35
BP Oil Corp.		
Port Arthur, Jefferson	1972	35
Gulf Oil Corp.		
Port Arthur, Jefferson	Before 1961	75
Expansion	1962	+75
Mobil Oil Corp.		
Beaumont, Jefferson	Before 1962	50
American Petrofina		
Mount Pleasant, Titus	1969	16
UTAH		
Chevron Oil Co.		
Salt Lake City	1972	12
VIRGINIA		
American Oil Co.		
Yorktown, York	1957	50
WISCONSIN		
Murphy Oil Corp.		
Superior, Douglas	1972	15

(a) Represents plant capacity in April, 1973.

TABLE 6. CLAUS SULFUR PLANT CAPACITY FOR RECOVERING REFINERY SULFUR(a)--Metric Tons Per Day

State	Total Crude Capacity,(b) 10^3 MT/D(20)	Sulfur Capacity,(c) MT/D(11)
Alabama	5.31	--
Alaska	7.33	9
Arkansas	6.55	25
California	234.60	2,510
Colorado	6.76	18
Delaware	19.15	775
Florida	0.68	--
Georgia	1.68	--
Hawaii	8.66	--
Illinois	142.48	569
Indiana	73.54	414
Kansas	52.94	44
Kentucky	21.68	--
Louisiana	212.21	570
Maryland	3.27	--
Michigan	18.11	89
Minnesota	23.71	170
Mississippi	41.90	30
Missouri	14.09	80
Montana	18.95	113
Nebraska	0.68	--
New Jersey	80.98	617
New Mexico	6.46	30
New York	14.04	50
North Dakota	7.22	200
Ohio	79.89	89
Oklahoma	63.12	--
Oregon	2.26	--
Pennsylvania	88.63	342
Rhode Island	1.03	--
Tennessee	3.97	--
Texas	477.10	1,178
Utah	16.59	12
Virginia	6.57	50
Washington	46.39	--
West Virginia	2.67	--
Wisconsin	4.86	15
Wyoming	19.53	--
TOTAL	1,835.59	7,999

(a) Does not include standby capacity.
(b) 1 metric ton is taken to be 7.31 barrels of oil.
(c) Sulfur capacity as of April, 1973.

$$H_2S + 1/2\ O_2 \rightleftarrows H_2O + S,\ \Delta H = 21{,}000\ \text{cal/g-mole}\ H_2S \qquad (1)$$

$$H_2S + 3/2\ O_2 \rightleftarrows SO_2 + H_2O,\ \Delta H = 61{,}900\ \text{cal/g-mole}\ H_2S \qquad (2)$$

$$2H_2S + SO_2 \rightleftarrows 3/8\ S_8 + 2H_2O,\ \Delta H = 12{,}400\ \text{cal/g-mole}\ H_2S. \qquad (3)$$

Considerable information has been written about Claus plants and Claus plant technology(12-19) and is not reviewed in detail here. Briefly, in this process, sufficient air to convert all the H_2S to sulfur is added to the acid-gas stream, and the gases enter the acid-gas burner and reaction chamber. The H_2S and oxygen react by way of Reaction (1) above and produce sulfur vapor. Temperatures in the burner here will be close to 1100 C. As much as 50 to 60 percent conversion of the hydrogen sulfide to sulfur may take place in this reaction chamber.

Some SO_2 will also be formed. Most of the heat generated in the burner and reaction chamber is removed in the waste-heat boiler by generating high-pressure steam. The gas is cooled to about 320 to 370 C. The gases are cooled further in the sulfur condenser, to about 150 C, and the sulfur is condensed and drained to storage. Low-pressure steam is generated in the condenser.

The gases are reheated by a hot-gas bypass and introduced into the first catalytic converter at about 230 to 260 C. The bauxite catalyst is used in the converter where the Claus reaction [Reaction (3)] occurs. From the first catalytic converter, the effluent gas is cooled to about 150 C in a condenser where more low-pressure steam is generated. Liquid sulfur is drained to storage and the remaining acid gases are reheated (230 to 260 C) and passed through the second catalytic converter, followed by a sulfur condenser. Liquid sulfur is removed and low-pressure steam is generated. If desired, the tail gas can be further treated by one of several processes to reduce tail-gas emissions to less than 0.1 percent of the incoming sulfur.

The above-mentioned two-stage process permits sulfur recoveries as high as 96 percent. Some three-converter plants of recent design achieve 98 percent recoveries. The installation of the third converter is justified only in large sulfur plants. Typical compositions for the gas streams entering and leaving a hypothetical 100 MT/D refinery Claus plant are shown in Table 7.(21)

TABLE 7. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING HYPOTHETICAL 100-MT/D REFINERY CLAUS PLANT

Basis: Sulfur Recovery in Claus Unit of 94 percent[(a)]

Composition, percent volume	Claus Intake	Claus Tail Gas Before Incineration	Claus Tail Gas After Incineration[(b)]
H_2S	89.9	0.85	--
SO_2	--	0.42	1.08
S vapor and mist	--	0.05	--
COS	--	0.05	--
CS_2	--	0.04	--
CO	--	0.22	--
CO_2	4.6	2.37	4.23
HC (MW: 30)	0.5	--	--
H_2	--	1.60	--
H_2O	5.0	33.10	26.57
N_2	--	61.30	66.68
O_2	--	--	1.44
TOTAL	100.0	100.00	100.00
Temperature, C	40	140	650
Pressure, atm	1.45	1.26	1.00
Gas quantity (relative amount) moles	1	3.0	5.0
Flow,[(c)] scmm	56.78	170.35	284.48

(a) Taken from Reference 21.

(b) Based on using 10 percent excess air in the incinerator and CH_4 as fuel.

(c) Flow given in standard cubic meters per minute (scmm).

Under the conditions prevailing in the reaction furnace (approximately 1100 C), formation of some carbonyl sulfide (COS) and carbon disulfide (CS_2) is inevitable if the acid gas contains CO_2 and hydrocarbons:

$$CO_2 + H_2S \rightleftarrows H_2O + COS \qquad (4)$$

$$COS + H_2S \rightleftarrows H_2O + CS_2 \qquad (5)$$

$$CH_4 + 3S \rightarrow H_2S + CS_2 \qquad (6)$$

Although the amounts of COS and CS_2 formed are relatively small (about 400 to 500 ppm each under equilibrium conditions), especially if the hydrocarbon content of the acid gas is low, they are significant as potential air pollutants. Under circumstances where kinetic factors control the formation of COS and CS_2, concentrations can be much higher, i.e., perhaps as high as 4000 ppm COS plus CS_2, depending upon temperature. Also, some CO and H_2 are formed by partial oxidation of hydrocarbons contained in the Claus feed gas.

A special catalyst may be placed in one or all of the catalytic converters to hydrolyze COS and CS_2 to H_2S and CO_2 by reversing Reactions (4) and (5) at the lower converter temperatures (approximately 260 C), thus minimizing the formation of these compounds. The modified process emphasizes maximum conversion efficiency (about 99 percent sulfur recovery) in an effort to minimize expenditure for tail-gas desulfurization.

Liquid-Phase Oxidation of H_2S to Elemental Sulfur

In the Claus process, sulfur in the minus-two oxidation state (H_2S) is converted to the zero oxidation state (elemental sulfur). This is done by partially burning the H_2S (-2 oxidation state) to yield one-third of the original H_2S stream on a molar basis in the form of SO_2 (+4 oxidation state) and then catalytically reacting SO_2 with the remaining two-thirds H_2S. Sulfur dioxide can, in this case, be viewed as the oxygen carrier. In a number of other processes specifically designed to handle low concentrations of sulfur compounds, as in refinery fuel gas, the oxygen carrier is either an organic or inorganic compound chosen for its ease of transferring oxygen to the species being oxidized (H_2S) and for ease of reoxidation in a recycling process. This is the principal characteristic of the anthraquinone and naphthaquinones used in such processes as the Stretford[(22)] and Takax[(23)] methods of desulfurizing fuel gas, and two tail-gas-treating processes incorporating the Stretford process; namely, the Beavon[(24,25)] and Cleanair[(26)] processes. Inorganic arsenical oxygen carriers are used in the Thylox[(27)] and Giammarco-Vetrocoke[(28)] methods. Iron oxide plays a similar role in the Ferrox[(29)], Manchester[(30)], and old iron-sponge techniques[(31)].

Two of the leading oxygen-carrier processes are described below: the Stretford process, which is characteristic of an organic oxygen carrier, and the Giammarco-Vetrocoke-H_2S (G-V) process, which is characteristic of an inorganic oxygen carrier. Both processes have been used widely for desulfurizing natural gas and refinery gases in Europe, but are little known in the United States. The G-V and Stretford processes are classic examples of multiple, coupled redox reactions in solutions. Only one known plant uses the G-V process in the United States (a natural gas plant in Texas), while the Stretford process is being applied to treating natural, refinery, and industrial gases.

Stretford Process. The Stretford process, shown in Figure D-1, is a one-step process to convert low-concentration hydrogen sulfide to elemental sulfur.[(32-34)] The refinery fuel gas is passed into a countercurrent column where the fuel gas is quenched and the H_2S is absorbed in the Stretford solution. The Stretford solution has the following constituents:

- Anthraquinone disulphonic acid (ADA) - The 2:7 isomer of ADA oxidizes 4-valent vanadium to 5-valent.
- Sodium meta vanadate - When reacted with HS^-, vanadium reduces from 5-valent to 4-valent, resulting in the precipitation of sulfur.
- Sodium potassium tartrate (Rochelle Salt) - Prevents deposition of vanadium in overloaded (upset) solutions.
- Soda ash - When carbon dioxide is present in the gas stream a mixture of sodium carbonate and sodium bicarbonate is formed, giving a solution of stable pH normally in the range of 8.5 to 9.5. This provides the alkaline solution for initial H_2S removal from the

gas stream with the formation of hydrosulfide. In the absence of CO_2, the solution pH is controlled by use of a buffer such as sodium borate.

- Bellasol - An EDTA compound that sequesters solubilized iron in the solution.

The H_2S is absorbed by the active Stretford solution, and the clean fuel gas is used for process purposes. Outlet sulfur loadings depend on design but are usually guaranteed to be less than 1 ppmv (sulfur as H_2S) and usually run about 0.2 ppm in certain applications. About 25 Stretford plants are operating in Great Britain and Northern Ireland where the maximum level of H_2S permitted is 1.5 ppm. Most of these plants have demonstrated on a continuous basis exit loadings of less than 1 ppm. A partial list of Stretford units treating refinery gases is given in Table 8.

The Stretford solution, after recirculation through the hydrogen sulfide absorber, is retained in a holding tank for 10 minutes to allow for completion of the sulfur precipitation. The Stretford solution is then regenerated by air blowing and the reduced vanadium is restored to the 5-valent state through a mechanism involving oxygen transfer via the ADA.

The sulfur formed in the Stretford process is finely divided and is floated to the top of the oxidizer by the air. The sulfur forms a froth containing 6 to 8 percent sulfur at the top of the oxidizer. This froth overflows to a settling tank where the sludge is accumulated and fed to a rotary vacuum filter. Underflow from the oxidizer is sent to the absorber pump tank for recirculation to the H_2S absorber.

The sulfur cake is fed to an autoclave where heat is applied to melt the sulfur. The sulfur-water mixture is separated, and marketable liquid sulfur of greater than 99 percent purity is obtained.

The reactions upon which this process is based are essentially insensitive to pressure. Operating temperatures throughout the unit are in the range of ambient to 50 C. The reactions are summarized below:

TABLE 8. PARTIAL LIST OF EXISTING STRETFORD PLANTS TREATING REFINERY GASES FOR SULFUR REMOVAL(a)

Plant Location	Type Gas	Feed, scmd	H_2S Inlet Loading, ppm
Reading, U.K.	Reformed refinery gas	0.73×10^6	100
Southampton, U.K.	Reformed refinery gas	0.56×10^6	100
Antwerp, Belgium	Refinery	1.26×10^6	5,000
Belfast, N. Ireland	Refinery/reformed	1.37×10^6	16,200
Toledo, Ohio(b)	Refinery	1.37×10^6	19,500
Long Beach, Calif.(c)	Petroleum gas	1.54×10^6	1,500

(a) Numerous Stretford units have been installed throughout the world for treating natural gas and a variety of industrial gases. In addition, several Stretford units have been incorporated into the Cleanair and Beavon tail-gas-treating processes.

(b) Sun Oil Company.

(c) THUMS project operated by the Lomita Gasoline Company.

(1) Absorption of H_2S

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \ .$$

(2) Precipitation of sulfur

$$2NaVO_3 + NaHS + NaHCO_3 \rightarrow S\downarrow + Na_2V_2O_5 + Na_2CO_3 + H_2O \ .$$

(3) Regeneration of sodium vanadate

$$Na_2V_2O_5 + \text{ADA (oxidized)} \rightarrow 2NaVO_3 + \text{ADA (reduced)} \ .$$

(4) Regeneration of ADA

$$\text{ADA (reduced)} + \tfrac{1}{2}O_2 \text{ (air)} \rightarrow \text{ADA (oxidized)} \ .$$

(5) Overall reaction

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S\downarrow + H_2O \ .$$

COS and CS_2 are not recovered by the Stretford process and this reduces the overall sulfur recovery. Otherwise, the Stretford solution quantitatively removes H_2S. Some adverse side reactions occur, owing to peaks in loading (increased liquor temperature) and trace oxidizing gases contained in the fuel gas (notably oxygen, SO_2, and HCN), and these result in the buildup of sodium thiosulfate and related compounds which must be purged from the system. A typical analysis for the purge stream is shown in Table 9.(35) The rate of thiosulfate formation depends on the partial pressure of oxygen in the inlet gas stream and on the pH and temperature of the liquor. Formation of thiosulfate is quite low, below about 40 C.

Currently, the Stretford purge stream normally is disposed of by discarding it to an industrial sewer. A process alternative that is being developed by Nittetu Chemical Engineering (NICE), Ltd., involves treatment to reclaim the sodium value as Na_2CO_3(36) (see Figure 5). As shown in the diagram, waste liquid removed from the desulfurization plant is first fed to the evaporator operated at 60 C and a vacuum of 100 mm Hg (abs), where the salts are preconcentrated to about 50 weight percent. The evaporator heat source is quenched combustion gas obtained directly from the quenching tank at a temperature of about 90 C.

TABLE 9. TYPICAL COMPOSITION (Weight Percent) OF STRETFORD PURGE SOLUTION[a]

Na_2CO_3	0.47
Na ADS[b]	0.07
Na meta vanadate	0.03
Na citrate	0.03
$Na_2S_2O_3$	0.60
NaSCN	0.60
H_2O	98.20

(a) Purge solution approximately 0.0125 to 0.125 l/g-mole of feed gas to the absorber.

(b) Sodium anthraquinone disulfonate.

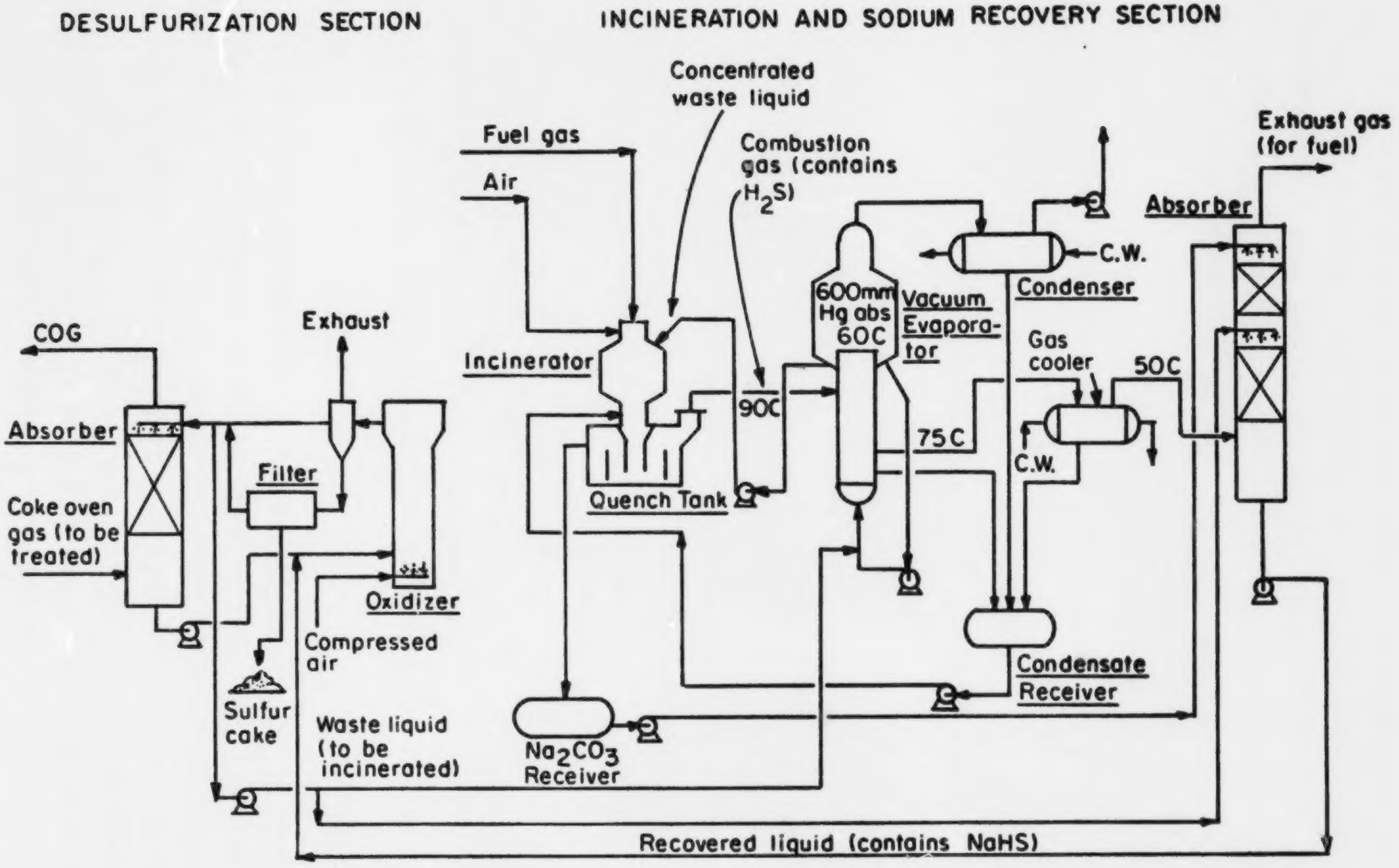

DESULFURIZATION SECTION
INCINERATION AND SODIUM RECOVERY SECTION
COG
Absorber
Coke oven gas (to be treated)
Exhaust
Filter
Oxidizer
Compressed air
Sulfur cake
Waste liquid (to be incinerated)
Fuel gas
Air
Incinerator
Concentrated waste liquid
Quench Tank
Combustion gas (contains H_2S)
90C
600mm Hg abs
60C
Vacuum Evaporator
75C
Na_2CO_3 Receiver
Condenser
C.W.
Gas cooler
C.W.
50C
Condensate Receiver
Absorber
Exhaust gas (for fuel)
Recovered liquid (contains NaHS)

FIGURE 5. TREATMENT OF STRETFORD PROCESS PURGE SOLUTION(36)

The concentrated waste liquid is then sprayed into the incinerator. Combustion of an auxiliary gas maintains the incinerator at 850 C in a reducing atmosphere. The reducing conditions are maintained by limiting the oxygen feed at 70 to 80 percent of the theoretical amount required for combustion. At the designated residence time, most of the sodium salts decompose to Na_2CO_3 and $NaHCO_3$; they are then blown into the quenching tank along with the hot combustion gas.

The quenching tank carries out two tasks: quenching of the hot combustion gas that is blown from the incinerator, and the capture of sodium salt contained in the gas, mainly Na_2CO_3. Quench and makeup water for the reconstituted Na_2CO_3 solution is fed through the gas-blowing duct between the incinerator and the quenching tank. The Na_2CO_3 solution is continuously removed from the tank and used as absorbent in the H_2S absorber.

The combustion gas, with sodium salts removed, is drawn out of the tank at approximately 90 C. This gas contains about 8 volume percent (dry basis) of H_2S as well as such gases as H_2, CO, and CH_4 and has a temperature of about 75 C when discharged from the shell side of the evaporator. It is cooled to about 50 C by a surface condenser and cooler before being supplied to the H_2S absorber.

The absorber is designed to return the absorbed H_2S that results from incineration under the reducing condition to the oxidizer at the desulfurization plant. There it is recovered from the filters as elemental sulfur. For this reason, the Na_2CO_3 solution, recovered from the quenching tank, and the absorbent from the desulfurization plant are both recovered. As far as is known, the NICE process has been tried only at the pilot-plant level.

Giammarco-Vetrocoke (H_2S) Process. The Giammarco-Vetrocoke H_2S removal process (see Figure D-2) is based on the absorption and reaction of hydrogen sulfide in alkaline arsenites and arsenates.(37,38) It is older, and the precursor of the Stretford process, since it involves coupled redox reactions in solution.

Elemental sulfur is formed from arsenic-activated sodium carbonate solution. The chemistry of the H_2S-removal process is quite complex but can be represented by the following reactions:

Absorption

$$Na_3AsO_3 + 3H_2S \rightleftarrows Na_3AsS_3 + 3H_2O. \qquad (1)$$

Digestion

$$Na_3AsS_3 + 3Na_3AsO_4 \rightleftarrows 3Na_3AsO_3S + Na_3AsO_3. \qquad (2)$$

Acidification and Precipitation

$$Na_3AsO_3S \rightarrow Na_3AsO_3 + S. \qquad (3)$$

Oxidation

$$Na_3AsO_3 + 1/2\ O_2 \rightarrow Na_3AsO_4. \qquad (4)$$

Overall Reaction

$$H_2S + 1/2\ O_2 \rightarrow S + H_2O. \qquad (5)$$

Sour gas enters the base of the absorber column at pressures up to 75 atmospheres. The absorption (1) is extremely rapid, with equilibrium partial pressures over the solution so low that treated gases containing less than 1 ppm are readily achieved. The absorption step is followed by the digestion step (2) which stabilizes the sulfur in a form unaffected by CO_2 and oxygen. One mole of oxidized activator must be in the solution per mole of absorbed sulfur to permit the digestion step to proceed. The thioarsenite ($Na3AsS3$) formed is slowly converted to mono-thioarsenate ($Na3AsO3S$) and arsenite ($Na3AsO3$), Reaction (2), which occurs in the absorber and in the subsequent oxidizing column. The mono-thioarsenate formed ($Na3AsO3S$) in Reaction (2) has an even lower vapor pressure of $H2S$. Mono-thioarsenate ($Na3AsO3S$), being more soluble, helps keep the sulfur in solution.

The solution leaving the base of the absorber passes to an air-blown oxidizing column working at atmospheric pressure and around 40 C. The vessel is open to the atmosphere at the top. Under the oxidizing conditions, the mono-thioarsenate (Na_3AsO_3) decomposes to arsenite (Na_3AsO_3) and elemental sulfur by Reaction (3). Elemental sulfur is removed overhead from the oxidizer by froth flotation, vacuum filtered, and washed. The oxygen-transfer reaction [Reaction (4)] reestablishes the original Vetrocoke solution balance by oxidizing some arsenite (Na_3AsO_3) to arsenate (Na_3AsO_4).

The Giammarco-Vetrocoke H_2S process has been used in the European natural gas industry and it could be adopted to refinery gases. Its main disadvantage is that the arsenate and arsenite solutions must be handled. Consequently, it is being largely replaced by less toxic solutions like the Stretford purge solution.

One of the latest in a series of processes based on multiple, coupled, redox reactions is the Cataban process.(39) The process is based on an oxidation-reduction system where a complexed polyvalent ion, preferably ferric ion, kept in aqueous solution by an organic chelating agent, oxidizes hydrogen sulfide to sulfur, the ferric iron being reduced to the ferrous state. Simultaneously, atmospheric or other oxygen reoxidizes the ferrous iron complex to ferric iron. The redox reactions involved may be represented by the following.

Oxidation by Hydrogen Sulfide to Elemental Sulfur

$$(1)\quad 2Fe^{+++} + H_2S \;=\; 2Fe^{++} + S + 2H^{+}.$$

Regeneration of Ferric Ion

$$(2)\quad 2H^{+} + 2Fe^{++} + 1/2\ O_2 \;=\; 2Fe^{+++} + H_2O.$$

Overall Reaction for the Two Steps

$$(3)\quad H_2S + 1/2\ O_2 \;=\; S + H_2O.$$

TAIL-GAS-PROCESSING TECHNOLOGY FOR CLAUS SULFUR PLANTS

Tail-gas-processing concepts that have been tested and are being operated or installed in conjunction with refinery Claus plants are listed in Table 1. These methods, with modification, probably represent today's most practical technology for large "clean-up" units for treating tail gas. Flow diagrams for all of these processes are presented in Appendix E. In this section of the report, the following seven processes are described in detail:

(1) Beavon
(2) Cleanair
(3) Wellman-Lord
(4) Shell Claus Off-Gas Treatment (SCOT)
(5) Institut Francais du Petrole Processes
    (IFP-1500 and IFP-150)
(6) Chiyoda Thoroughbred 101
(7) Sulfreen.

Tail gas from a two-stage Claus sulfur-recovery unit can be expected to contain some 7,000 to 12,000 ppm of sulfur compounds (see Table 7). These compounds are H_2S, SO_2, CS_2, COS, and S_x (expressed as S_8). Tail-gas-cleaning processes may be classified as continuations of the Claus reaction or as add-on processes of a different nature. The Beavon, Cleanair, IFP, and Sulfreen processes are of the first type and involve continuation of the Claus reaction. The Wellman-Lord, SCOT, and Chiyoda processes are examples of add-on processes that are not based on the Claus reaction. The Wellman-Lord SO_2 recovery process and the Chiyoda process handle tail gas following its incineration in the sulfur-recovery plant, i.e., the sulfur in the form of SO_2. The Beavon and Cleanair processes are similar in that the tail gas is handled in such a manner that the residual sulfur values occur as hydrogen sulfide which is then converted to sulfur in a Stretford unit. The IFP and Sulfreen processes use different catalysts to extend the Claus reaction--in the first process, in an organic liquid solvent using alkali metal salts as a catalyst, and in the second process, in the absorbed phase on the surface of either an alumina or activated carbon catalyst.

For each of the tail-gas processes under consideration, this review provides the following information:

(1) Process description

(2) Commercial status as measured by the number of units being used at refinery Claus sulfur plants

(3) Material balances, utility requirements, and waste streams generated in a tail gas unit applied to a typical 100-MT-D refinery Claus plant.

In almost all cases, the tables summarizing the number of commercial units in operation or under construction represent partial lists. For the most part, these data were obtained from the process vendors. However, it was difficult to keep such lists current and omissions are sure to have occurred. The material balances were generated for the tail gas as it progressed through the process under consideration by making various assumptions that were felt to be valid and commensurate with the unit operations involved. Although the material balance calculations should be fairly representative of gas compositions expected in the process, they are not rigorous in the sense that each flow stream (both liquid and gas) is completely defined and satisfies conservation of mass. Since this was the case, the utilities requirements were not obtained from material and energy balances as one would normally do when performing design calculations. Rather, they represent best guesses obtained from the available information and a knowledge of the process. This often involved comparing several sources of data (vendor estimates, open literature, and data obtained from process users) and then selecting the one thought to be most reliable.

For the sake of consistency in performing the material balance calculations and for making process comparisons, the following ground rules were set.

(1) The Claus plant being treated was 100 MT/D.

(2) The tail gas being treated had the characteristics given in Table 7.

(3) Incineration and stack gas reheating were performed using methane.

(4) Incineration was done in the existing Claus-plant incinerator at a temperature of 650 C.

(5) Stack-gas reheating for processes based on SO_2 absorption was done in a direct-fired reheater with the exit temperature to the stack being 316 C.

Beavon Process

Process Description. The Beavon process$^{(25)}$ (see Figure E-1) begins by converting substantially all of the sulfur present in the tail gas before incineration (i.e., SO_2, COS, CS_2, and elemental sulfur) back to hydrogen sulfide. This is done by hydrogenation under very moderate conditions of temperature and pressure, resembling those in the Claus plant. Before the tail gas enters the packed-bed hydrogenation reactor, fuel gas is combusted substoichiometrically in air and steam (optional) in an inline burner. The combustion products are mixed with the tail gas to provide a reducing atmosphere. The burner operates fuel-rich, so it is possible to make extra hydrogen as required to supplement the hydrogen already in the tail gas. The hydrogenation reactions are catalyzed by a cobalt molybdate catalyst in the packed-bed reaction. The presence of this catalyst also promotes the reaction of water vapor with carbon monoxide to form hydrogen, or the reaction of water vapor with COS and CS_2 to form H_2S. The reactions thought to occur in the decomposition are:

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$

$$CS_2 + H_2O \rightleftarrows H_2S + COS$$

$$CS_2 + 2H_2S \rightleftarrows CH_4 + 3S$$

$$4H_2 + CS_2 \rightleftarrows 2H_2S + CH_4$$

$$COS + 4H_2 \rightleftarrows H_2O + H_2S + CH_4$$

After hydrogenation, the tail gas is cooled and water is removed in a direct-contact heat exchanger. The condensate is not corrosive, and is suitable for cooling-tower makeup after H_2S has been stripped out. A typical hydrogenation-reaction product gas contains 20,000 to 40,000 ppm of H_2S. This stream is fed at about 1.068 atm (1 psig) into the Stretford circuit for removal of hydrogen sulfide. (See description of the Stretford process presented earlier.) Tail gas from the Stretford unit is discharged to the atmosphere after incineration in the Claus plant incinerator.

Commercial Status. The Beavon process was developed jointly by the Union Oil Company and the Ralph M. Parsons Company. A partial list of Beavon units that are either operating or under construction is presented in Table 10. Eight units for which information was readily available are listed in Table 10. Two other units are believed to have been ordered.

Material Balance and Utilities. The Beavon process appears capable of treating Claus-plant tail gas to the 100 to 200-ppm level prior to incineration. Sulfur removal in the Stretford tower should be virtually quantitative for H_2S. Only the equilibrium COS and CS_2 values present in the gas stream following the catalytic reduction step and trace quantities of H_2S should be present and exhausted to the incinerator. Consequently, overall sulfur recovery from the Claus plant the tail gas would exceed 99.8 percent. Approximate sulfur-balance calculations are summarized in Table 11 for a hypothetical 100-MT/D Claus sulfur plant equipped with a Beavon unit. The compositions of the tail gas as it is processed through the catalytic reduction, quench tower, Stretford unit, and incinerator are given in Table 12. These figures formed the basis for the sulfur balance summarized in Table 11. Approximate utilities requirements for the process are given in Table 13.(24,40)

Waste Streams. Two waste streams are generated by the Beavon process. Neither is considered to be a significant secondary source of pollution (see Table 11 and Figure C-1). These are the sour-water condensate obtained by cooling the tail gas in the direct-contact heat

TABLE 10. PARTIAL LISTING OF ANNOUNCED BEAVON-STRETFORD TAIL GAS TREATING UNITS FOR REFINERY CLAUS PLANTS

Company/Location	On-Stream Date	No. of Units	Number/Capacity of Claus Plants, MT/D
Union Oil Company/ Wilmington, California	July, 1973	2	2/100
Mobil Oil Company/ Torrance, California	July, 1973	2	3/100
Atlantic-Richfield/ Philadelphia, Pennsylvania	September, 1973	1	1/140
Getty Oil Company/ Delaware City, Delaware	November, 1973	1	1/300
Kobe Steel Co./Japan	October, 1973	1	1/220
Texaco, Inc./ Long Beach, California	March, 1974	1	--
Unknown/ Carribbean	April, 1974	2	--
Union Oil Co./ Rodeo, California	November, 1974	3	--

TABLE 11. APPROXIMATE SULFUR BALANCE AND WASTE STREAMS FOR BEAVON TAIL-GAS PROCESS

I. Basis

A. 100 MT/D Claus plant

B. 94 percent sulfur removal in Claus plant

C. Assumed reduction of 85 percent each of COS and CS_2 to H_2S and treating to less than 10 ppm H_2S leaving Stretford tower. No affinity of COS and CS_2 for Stretford solution.

II. Sulfur Balance

A. Claus Plant

Input - 104.471 MT/D
Recovered - 98.203 MT/D
Tail gas - 6.268 MT/D

B. Beavon Process

Input - 6.268 MT/D
Recovered - 6.198 MT/D
Purge - 0.005 MT/D
Off-gas - 0.065 MT/D

III. Waste Streams

A. Sour-Water Condensate

1. pH - slightly acidic
2. H_2S and CO_2 dissolved to about 50 ppm each
3. Flow rate - about 0.72 l/sec for a Beavon tail-gas unit applied to a 100-MT/day Claus unit
4. Treatment - neutralized in wastewater-treatment system

B. Stretford Purge Solution

1. Composition - see Table 9 for approximate composition
2. Flow rate - approximately 0.0125 to 0.125 l/gram-mole of feed to the Stretford Tower, i.e., about 0.0126 to 0.126 l/sec for a unit serving a 100-MT/day Claus plant
3. Treatment - sent to refinery waste-treatment system or an industrial sewer

TABLE 12. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING 100-MT/D REFINERY CLAUS PLANT PLUS BEAVON TAIL-GAS PROCESS

(Basis: Sulfur recovery in Claus unit of 94 percent)

			Tail Gas			
Item	Intake	Tail Gas	After Reduction Reactor	After Quench Tower	Leaving Stretford	Off-Gas Following Incineration
Composition(a)						
H_2S	89.9	0.85	1.54	2.13	10 ppm	-
SO_2	-	0.42	0.00	0.00	0.00	165 ppm
S vapor and mist	-	0.05	0.00	0.00	0.00	-
COS	-	0.05	53 ppm	73 ppm	75 ppm	-
CS_2	-	0.04	53 ppm	73 ppm	75 ppm	-
CO	-	0.22	0.20	0.28	0.29	-
CO_2	4.6	2.37	3.18	4.39	4.49	5.87
HC (MW: 30)	0.5	-	0.06	0.08	0.08	-
H_2	-	1.60	0.21	0.29	0.30	-
H_2O	5.0	33.10	32.30	6.45	6.59	9.88
N_2	-	61.30	62.50	86.36	88.24	83.70
O_2	-	-	0.00	00.00	0.00	0.52
Total	100.0	100.00	100.00	100.00	100.00	100.00
Temperature, C	40	140	400	38	38	650
Pressure, atm	1.45	1.26	1	1	1	1
Gas Quantity (Relative Amount), moles	1.00	3.00	3.28	2.45	2.39	3.40
Flow(a), scmm	56.78	170.35	191.94	139.19	135.94	193.06

(a) Percent by volume, unless otherwise noted.

(b) Flow given in standard cubic meters per minute (scmm).

TABLE 13. ESTIMATE OF UTILITIES REQUIRED FOR BEAVON TAIL-GAS PROCESS FOR 100-MT/D CLAUS SULFUR PLANT

Item	Value
Steam (3.40 atm, sat), kg/hr	1453[(a)]
Cooling Water, l/sec	22.7
Electricity, kwr/hr	250
Fuel Gas, scmh	224[(c)]
Boiler feed water, l/sec	0.25
Chemicals	
Stretford Solution, l/sec	0.0131 - 0.131
Catalyst	
Operating Labor, men/shift	1/3 - 1/2
Maintenance, % of FCI	5

(a) Steam produced in the process.

(b) Fuel gas rated at 9000 kg-cal/cu m.

(c) Approximately 13 percent of the fuel gas is consumed in heating the tail gas prior to the reduction reactors, and 87 percent is used in incinerating the off-gas prior to sending it to the atmosphere.

exchanger prior to entry to the Stretford tower and the purge stream from the oxidizing unit following the Stretford tower. The size and character of these waste streams are described in Table 11. The condensate removed would be slightly acidic due to H_2S and CO_2 absorption (perhaps 50 ppm each) and would be treated by neutralizing in the refinery waste-treatment system. The Stretford purge stream (see Table 9) would be sent to either the refinery waste-treatment system or to an industrial sewer.

Cleanair Process

Process Description. The Cleanair process(26) includes the Stretford process and two new processes developed by the J. F. Pritchard Company and the Texas Gulf Sulfur Company. Similar to the Beavon process, one of the features of the Cleanair process is the removal of organic sulfur compounds (COS and CS_2).

Although little good technical information is available in the open literature and the J. F. Pritchard Company appears to be extremely secretive about process details, an attempt was made to draw a schematic flow diagram for the process (see Figure E-2). The Claus tail gas is fed to a fixed-bed reactor which contains both a reduction catalyst (thought to be Co/Mo) and a hydrolysis catalyst (unknown). In this reactor, termed Stage III by Pritchard, hydrolysis reduction of COS and CS_2 to H_2S takes place. The reactions thought to be occurring are:

$$CS_2 + H_2O \rightleftarrows COS + H_2S$$

$$COS + H_2O \rightleftarrows H_2S + CO_2 \quad .$$

The Stage III fixed-bed catalyst can be incorporated directly into the Claus plant, usually in the first-stage reactor, while it operates on tail gas in existing units as shown in Figure E-2.

Carbon dioxide also is decomposed to CO in the fixed-bed reactor to prevent the reoccurrence of COS. The treated tail gas is cooled in a quench tower prior to the Stage I reactor. Since the Claus reaction is thermodynamically favored at low temperature, some additional vapor-phase sulfur is formed during this process. The cooled gas is fed into a packed reactor (Stage I) where SO_2 as well as some H_2S are absorbed and converted to elemental sulfur via continuation of the Claus reaction:

$$2H_2S + SO_2 \overset{\text{cat.}}{\rightleftarrows} 3S + H_2O \quad .$$

Although details regarding the chemical nature of the solution being used in Stage I are proprietary, it is thought to be an aqueous medium having a catalyst and an oxygen carrier to promote the Claus reaction. The bottoms from the Stage I absorber-reactor are sent to a clarifier where sulfur is separated from the reaction solution as the underflow. A further separation takes place in an autoclave separator from which liquid sulfur is withdrawn as product. The aqueous phase from the autoclave separator is then recycled to the clarifier. A slip stream from the clarifier is sent to a depurator and oxygenated and sent back to the Stage I reactor. A purge stream is removed from the depurator and used as process water.

After Stage I, the tail gas is sent to a Stretford unit where H_2S is removed. The purified gas is then sent to a typical Claus incinerator where fuel and air are added to oxidize any residual sulfur to SO_2 and CO to CO_2 before it is discharged through the stack.

The Cleanair process should be capable of reducing to extremely low values the amount of sulfur being discharged in the tail gas. Values as low as 1 ppm should be possible, depending upon the efficiency of the hydrolysis reduction steps. Any COS and CS_2 not hydrolyzed would, of course, not be removed in either Stages I or III.

Commercial Status. The Cleanair process is licensed by the J. F. Pritchard Company. A partial list of five Cleanair units is shown in Table 14. The first commercial unit which treated Claus-plant tail gas was the unit built for Gulf Oil Company's Philadelphia, Pennsylvania refinery. It follows a 46-MT/D Claus plant. Because of recurrent operating problems, the Cleanair process at Gulf in Philadelphia, as well as the two other units in Los Angeles County, remain in start-up status. Two other units following Claus plants are under construction for Techmashimport in the U.S.S.R.

TABLE 14. PARTIAL LISTING OF ANNOUNCED CLEANAIR TAIL GAS PROCESSING UNITS FOR REFINERY CLAUS SULFUR PLANTS

Company/Location	On-Stream Date	No. of Units/ Capacity, scmm	Number/Capacity of Claus Plants, MT/D
Atlantic Richfield Corp. (ARCO)/ Wilmington, California	--	1/434	3/90
Gulf Oil Co./ Philadelphia, Pennsylvania	--	1/112	1/46
Santa Fe Springs Refinery (Gulf Oil Co.)/Santa Fe Spring, California	--	1/78	1/27
Techmashimport, U.S.S.R.	--	2/-	--

Material Balance and Utilities. Currently there exists a lack of information about the Cleanair process in the open literature. Also, the J. F. Prichard Company considers all information pertaining to the process as proprietary. Consequently, no meaningful material balances or estimates of utility requirements were possible.

Waste Streams. The only waste streams from the process would be the purge stream from the Stretford unit in Stage II, and the sour water purged from the depurator in Stage I. No quantitative information can be presented because of a lack of material-balance data.

Wellman-Lord Tail-Gas Process

Process Description. The Wellman-Lord process(41-43) uses a wet regenerative system to reduce sulfur concentration in stack gas to about 200 ppm (see Figure E-3). The sulfur constituents in the Claus-plant tail gas are oxidized to SO_2 in the incinerator, passed through a waste heat boiler, and then quenched to reduce the gas temperature to about 38 C and remove excess water. The SO_2-rich flue gas is then contacted countercurrently with a sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$) solution which absorbs SO_2 to form additional bisulfite. The absorber can be either a packed or tray column. Regenerated sulfite solution enters the top of the column and spent solution is discharged. The column is maintained at 38 C. The principal reaction between the SO_2 and the absorbent solution is

$$SO_2 + Na_2SO_3 + H_2O \rightleftarrows 2NaHSO_3 \quad .$$

The SO_2-rich solution is boiled by indirect heating in an evaporator-crystallizer using an external circulation loop. The conditions are approximately 110 C and 1.0 atm. About 9-10 kilograms of steam are used to evaporate each kilogram of SO_2. The choice of single-effect or double-effect evaporation generally depends on the steam costs. The bisulfite solution decomposes to SO_2 and H_2O gas and sodium sulfite precipitates out in the crystallizer according to the reaction:

$$2NaHSO_3 \xrightarrow{Heat} Na_2SO_3 + SO_2 + H_2O \ .$$

The sulfite crystals are removed from the evaporator circuit and redissolved for reuse as lean solution to the absorber.

The wet SO_2 gas flows to a partial condenser where the water is condensed and reused to dissolve the sulfite crystals. The enriched SO_2-H_2O vapor stream (85 percent/15 percent) is then recycled back to the Claus plant for conversion to elemental sulfur.

Apart from the two major reactions above, sodium sulfate (Na_2SO_4), which is nonregenerable in the normal process, is formed in the absorber as a result of solution contact with oxygen or sulfur trioxide as follows:

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$$

$$2Na_2SO_3 + SO_3 + H_2O \rightarrow Na_2SO_4 + 2NaHSO_3 \ .$$

The sodium sulfate so formed is controlled at a level of approximately 5 percent by weight in the absorber feed stream by maintaining a continuous purge from the system. This purge stream will be discussed later.

An additional source of sodium sulfate and thiosulfate is the auto-oxidation or so-called disproportionation reaction which takes place in the regeneration section:

$$6NaHSO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3 + 2SO_2 + 3H_2O \ .$$

A small amount of sodium pyrosulfite is also formed owing to the decomposition of sodium bisulfite:

$$2NaHSO_3 \rightleftarrows Na_2S_2O_5 + H_2O \ .$$

About 10 to 30 percent of the sodium values in the recirculating circuit are lost because of the purge stream (see Table 15). A process modification incorporates a centrifuge into the purge line to further concentrate purge solids in the slurry. With this modification, sodium losses can be reduced to 8 to 10 percent. In addition, any excess water removed by cooling the gas in the quench tower would be slightly acidic due to absorption of SO_2 and CO_2. This dilute acid would be purged and neutralized.

TABLE 15. APPROXIMATE COMPOSITION OF WELLMAN-LORD SO_2 PURGE STREAM[a]

Component	Weight Percent[b]
Total Dissolved Salts	26
Na_2SO_4	5
$NaHSO_3$	7
Na_2SO_3	14
$Na_2S_2O_3$	(c)
$Na_2S_2O_5$	(c)
Water	74

[a] No centrifuge in the system and water added to dissolve all solids.

[b] Data taken from letter to J. M. Genco, from C. B. Earl, Davy Powergas, Inc., Lakeland, Florida (December 13, 1973).

[c] Amount in solution is unknown but is thought to be about 1 percent by weight.

A makeup of caustic is required to replace that lost in the purge stream. The caustic makeup solution reacts with the sodium bisulfite in the absorber solution to form additional sodium sulfite:

$$NaOH + NaHSO_3 \longrightarrow Na_2SO_3 + H_2O \quad .$$

Soda ash (Na_2CO_3) can also be used as the makeup source of sodium.

Commercial Status. The Wellman-Lord process is licensed by The Davy Powergas Company of Lakeland, Florida. Data on eight units known to be in use in the United States and Japan for treating Claus tail gas(44) are summarized in Table 16. The Claus plants range in size from 80 to 290 MT/day. Since the process treats SO_2 gas, it also has found application in treating boiler flue gas and tail gas from sulfuric acid plants. In all, there are about 20 Wellman-Lord units either under construction or in operation.

Material Balance and Utilities. Approximate sulfur-balance calculations are given in Tables 17 and 18. The basic assumptions used in performing the material-balance calculations are:

(1) Virtually complete conversion of sulfur compounds to SO_2 in the incinerator
(2) Removal of SO_2 in the absorber to a level of about 250 ppm
(3) The off-gas from the SO_2 absorber is reheated to 316 C using 9000 kg-cal/cu m fuel gas
(4) Approximately 5 percent of the sulfur removed from the tail gas in the absorber is converted to nonregenerable forms of sulfur and must be purged from the system.

An estimate of the utilities requirements for a Wellman-Lord unit capable of handling the tail gas from a 100 MT/D Claus sulfur plant is shown in Table 19. These data, except for the caustic make-up requirements, were taken from information supplied by the Davy Powergas Company.(44) The caustic requirements were estimated from the material-balance calculations.

TABLE 16. PARTIAL LISTING OF ANNOUNCED WELLMAN-LORD TAIL-GAS PROCESSING UNITS

Company/Location	On-Stream Date	No. of Units/ Capacity, scmm	Number/Capacity of Claus Plant, MT/D
Standard Oil of California/ Richmond, California	January 1975	1/840	1/290
Kashima Oil Co./ Kashima, Japan	February 1974	1/532	1/180
Toa Nenryo/Arita, Japan	October 1974	1/952	2/150
Toa Nenryo/Matsushima, Japan	October 1974	1/280	1/80
Toa Nenryo Refinery/Kawasaki, Japan	August 1971	1/1,148	2/200
Standard Oil of California/El Segundo, California	September 1972	1/1,260	3/137
Standard Oil of California/El Segundo, California	January 1975	1/840	1/290
Standard Oil of California Richmond, California	August 1974	1/840	2/150

TABLE 17. APPROXIMATE SULFUR BALANCE AND WASTE STREAMS FOR WELLMAN-LORD TAIL-GAS PROCESS

I. Basis

A. 100 MT/D Claus Plant

B. 94 percent sulfur removal in Claus plant

C. Tail gas treated to 250 ppm SO_2 in Wellman-Lord off gas

II. Sulfur Balance

A. Claus Plant

Input - 104.471 MT/D
Recovered - 98.203 MT/D
Off-gas - 6.268 MT/D

B. Wellman-Lord Process

Input - 6.268 MT/D
Recovered - 4.853 MT/D
Off-gas - 0.134 MT/D
Purge - 1.281 MT/D

III. Waste Streams

A. Sodium Sulfate/Sulfite Purge - Evaporator Unit

1. Purge stream rate - 0.221 l/sec
2. Purge composition

Component	Percent by Weight
Na_2SO_4	5
$NaHSO_3$	7

3. Treatment - discharged to industrial sewer system. Davy Powergas is developing a proprietary process for treating this stream. Also, the NICE process developed for treating similar sodium waste streams should be applicable here.

B. Acid-Water Condensate

1. Purge Stream rate - 0.322 l/sec
2. pH 2
3. Treatment - neutralized in the refinery wastewater treatment system

TABLE 18. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING 100-MT/D REFINERY CLAUS PLANT PLUS THE WELLMAN-LORD TAIL-GAS PROCESS
(Basis: Sulfur recovery in Claus unit of 94 percent)

Item	Claus Intake	Claus Exhaust: Prior Incinerator	Claus Exhaust: After Incinerator	After Quench Unit	After Absorber	After Reheater[b,c] (Final Exhaust)
Composition[a]						
H_2S	89.9	.85	-	-	-	-
SO_2	-	.42	1.08	1.34	250 ppm	215 ppm
S vapor & mist	-	.05	-	-	-	-
COS	-	.05	-	-	-	-
CS_2	-	.04	-	-	-	-
CO	-	.22	-	-	-	-
CO_2	4.6	2.37	4.23	5.26	5.33	5.66
HC (MW: 30)	0.5	-	-	-	-	-
H_2	-	1.60	-	-	-	-
H_2O	5.0	33.10	26.57	8.76	8.88	9.80
N_2	-	61.30	66.68	82.85	83.98	82.43
O_2	-	-	1.44	1.79	1.81	2.11
Total	100.0	100.00	100.00	100.00	100.00	100.00
Temperature, C	40	140	650	43	43	316
Pressure, atm	1.45	1.26	1	1	1	1
Gas Quantity (Relative amount), moles	1	3.0	5.01	4.03	3.98	4.62
Flow[d], scmm	56.78	170.35	284.48	228.84	225.99	262.36

(a) Percent by volume unless otherwise noted.
(b) Direct fired reheat.
(c) May not need to reheat to 316 C.
(d) Flow given in standard cubic meters per minute (scmm).

TABLE 19. ESTIMATE OF UTILITIES REQUIRED FOR WELLMAN-LORD TAIL-GAS PROCESS FOR 100-MT/D SULFUR PLANT(a)

Item	Value
Steam (30.6 atm, sat.), kg/hr	(3,028)(b)
Cooling Water(c), l/sec	39.4
Electricity, kWr/hr	93
Fuel Gas(d), scmh	4,072(e)
Boiler Feed Water, l/sec	0.82
Chemicals (100% NaOH), MT/D	3.73
Operating Data	
Labor, men/shift	1/3-1/2
Maintenance, % FCI	5

(a) Letter to J. M. Genco from C. B. Earl, Davy Powergas, Inc. (December 13, 1973).

(b) Steam produced in process.

(c) Temperature rise of 17 C.

(d) Heating value taken to be 9000 kg-cal/cu m.

(e) Reheating done to 316 C with direct fired reheater.

Waste Streams. Two waste streams are generated in the Wellman-Lord tail-gas-cleaning process (see Table 17 and Figure E-3). These are acid-water condensate and a purge stream. The acid water is obtained by cooling and partially condensing water from the tail gas in the direct-contact heat exchanger prior to the SO_2 absorption tower. In the Wellman-Lord design, this waste stream amounts to about 0.32 l/sec for a 100-MT/D Claus plant and has a pH of approximately 2.(44) It is treated in the refinery wastewater-treatment system by neutralization with base.

The sodium sulfate/thiosulfate purge stream normally is removed as a slurry from the steam-stripping loop in the evaporator section of the process. It is dissolved in water to the approximate composition shown in Table 17 and sent to either an industrial sewer or the refinery wastewater-treatment plant if the latter is equipped to handle it. The purge following dissolution amounts to about 0.221 l/sec.(44) Currently, the Davy Powergas Company is developing proprietary technology for treating this stream. Also, the NICE process which treats similar waste streams to recover their sodium value as Na_2CO_3 would also appear to be applicable to the Wellman-Lord purge (see Figure 5).

Shell's Claus-Plant Off-Gas Treatment (SCOT) Process

Process Description. The SCOT Process(21,45,46) consists of a reduction section and an alkanolamine absorption section (see Figure E-4). The sulfur compounds together with free sulfur in the Claus tail gas are reduced to H_2S with hydrogen, or hydrogen together with carbon monoxide, over a cobalt/molybdenum catalyst (Shell catalyst S-534) at a temperature of about 300 C. Reducing gas can be supplied from an outside source (for example, reformer gas), or a suitable reducing gas can be generated in the direct heater. The heater is required in any case for heating process gas to the reactor inlet temperature. The reactor effluent is cooled in a waste-heat boiler to produce low-pressure steam and finally in a cooling tower to remove excess water vapor. The condensed water vapor from the process gas is sent to a sour-water stripper. The H_2S and some CO_2 are countercurrently removed by treating with di-isopropanolamine (DIPA) solution in an absorption column. The fat (DIPA) solution is regenerated by stripping H_2S in a conventional steam stripper. The regenerator off-gas, mainly H_2S and some CO_2, is recycled as feed to the first stage of the Claus unit. The absorber off-gas, which now contains about 300 ppmv H_2S, is incinerated in a standard Claus incinerator.

In the SCOT process, as in the Beavon process, COS, CS_2, and elemental sulfur can be removed effectively by reducing them to H_2S. SO_2 and elemental sulfur are reduced by H_2 as follows:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$S_8 + 8H_2 \rightarrow 8H_2S \ .$$

With an excess of H_2, virtually complete conversion of elemental sulfur and H_2S is obtained (i.e., residual SO_2 contents below 10 ppmv).

When carbon monoxide is also present as a reducing agent, the following additional reactions may occur:

$$SO_2 + 3CO \rightarrow COS + 2CO_2$$

$$S_8 + 8CO \rightarrow 8COS$$

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

$$CO + H_2S \rightleftarrows COS + H_2 \ .$$

Under normal conditions, the concentration of carbonyl sulfide (COS) approaches thermodynamic equilibrium (i.e., about 10 ppmv COS)

In addition to COS, carbon disulfide (CS_2) may also be present in Claus tail gases. CS_2 is converted over the Co/Mo catalyst to its equilibrium value (i.e., about 1 ppmv CS_2) as follows:

$$CS_2 + 2H_2O \rightleftarrows CO_2 + 2H_2S \ .$$

The Co/Mo catalyst has undergone a 4000-hour life test with hydrogen or a mixture of hydrogen/carbon monoxide as reducing agent. The results show that the reduction catalyst has a completely stable activity with residual SO_2 contents consistently below 10 ppmv.

Shell developed the SCOT process primarily for application to refinery Claus tail-gas treatment. Except for the Co/Mo reduction reactor and in-line burner, no additional equipment is required. If sufficient capacity exists, the overhead gas from the cooling (quench) tower can be recycled to the existing amine-treatment unit in the refinery. Thus, the process cycle can be completed without generating new waste-disposal problems. There would, of course, be normal degenerated amine solution to be disposed of. However, the SCOT process has still to be demonstrated on a commercial scale for a longer period before its feasibility can be fully evaluated.

Commercial Status. The SCOT process is being licensed by the Shell Development Company, Houston, Texas. Announced SCOT units in the United States and Canada(47) are listed in Table 20. Currently, the process is being applied to two rather small Claus plants--Champlin Petroleum Company in Wilmington, California (15 MT/D), and the Douglas Oil Company in Paramount, California (9 MT/D). Six other SCOT units have been ordered and are in various phases of construction. The largest unit has been ordered by Shell Canada for treating Claus tail gas at the Watertown Natural Gas Treating Plant, Alberta, Canada. The capacity of the Claus plant in this case is 2,100 MT/D.

Material Balance and Utilities. Approximate sulfur-balance calculations are summarized in Table 21. These estimates are based on the material balances presented in Table 22.(21) The basic assumptions in making the material-balance calculations are:

(1) Removal of H_2S in the absorption tower to a level of about 300 ppm

(2) The COS and CS_2 levels following reduction of sulfur compounds to H_2S in the Co/Mo reduction reactor are 10 ppm and 1 ppm, respectively.

TABLE 20. PARTIAL LISTING OF ANNOUNCED SCOT UNITS IN THE U. S. AND CANADA

(Total Claus Capacity = 2,900 MT/D)*

Company/Location	On-Stream Data	Number/Capacity of Claus Plants, MT/D
Champlin Petroleum Company/Wilmington, California	June, 1973	1/15
Douglas Oil Company/ Paramount, California	June, 1973	1/9
Shell Canada, Waterton Gas Treating Plant/ Alberta, Canada	December, 1974	1/2100
British Petroleum Standard Oil of Ohio/ Marcus Hook, Pennsylvania	October, 1974	1/160
U. S. Steel/ Clairton, Pennsylvania	Late 1974	--
Sun Oil Co./Duncan Oklahoma	Late 1974	--
Marathon Oil Co./ Detroit, Michigan		--
Murphy Oil Co./ Meraux, Louisiana	Late 1974	--
Shell Oil/Houston, Texas	Late 1974	--

* Claus plant units range in capacity from 9 MT/D to 2,100 MT/D.

TABLE 21. APPROXIMATE SULFUR BALANCE AND ESTIMATE OF WASTE STREAMS FOR SCOT TAIL-GAS PROCESS

I. Basis

A. 100-MT/D Claus plant

B. 94 percent sulfur removal in Claus plant

C. Tail gas treated to 300 ppm H_2S, 10 ppm CS_2, and 1 ppm COS in SCOT off-gas (prior to incineration)

II. Sulfur Balance

A. Claus plant

Input - 104.471 MT/D
Recovered - 98.203 MT/D
Off-gas - 6.268 MT/D

B. SCOT process

Input - 6.268 MT/D
Recovered - 6.188 MT/D
Off-gas - 0.080 MT/D

III. Waste Streams

A. Sour-Water Condensate

1. pH - slightly acidic
2. H_2S and CO_2 dissolved to about 50 ppm each
3. Purge rate - 0.442 to 0.631 l/sec
4. Treatment - send to sour-water stripper

B. Amine sludge - negligible

C. Spent reduction catalyst

TABLE 22. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING HYPOTHETICAL 100-MT/D REFINERY CLAUS PLANT PLUS SCOT TAIL-GAS PROCESS[a]

(Basis: sulfur recovery in Claus unit of 94 percent)

Item	Claus Intake	Claus Exhaust[a]	Scot Off-Gas	Incinerated Scot Off-Gas
Composition[b]				
H_2S	89.9	0.85	0.03	<10 ppm
SO_2	-	0.42	-	0.02
S vapor and mist	-	0.05	-	-
COS	-	0.05	10 ppmv	-
CS_2	-	0.04	1 ppmv	-
CO	-	0.22	-	-
CO_2	4.6	2.37	3.05	4.42
HC (MV: 30)	0.5	-	-	-
H_2	-	1.60	0.96	-
H_2O	5.0	33.10	7.00	9.84
N_2	-	61.30	88.96	83.94
O_2	-	-	-	1.78
Total	100.0	100.00	100.00	100.00
Temperature, C	40	140	40	650
Pressure, atm	1.45	1.26	1	1
Gas Quantity (Relative Amount), moles	1	3.0	2.2	3.5
Flow[c], scmm	56.78	170.35	124.91	198.74

(a) Prior to incinerator.

(b) Percent by volume unless otherwise noted.

(c) Flow given in standard cubic meters per minute.

Overall sulfur recovery in a two-stage Claus plant with the SCOT process should be in excess of 99.8 percent.

Table 23 presents an estimate of the utilities required for the SCOT process applied to a 100-MT/D Claus plant. These data were taken from Wall(48) and are essentially the same as those supplied by Shell Development Company.(47) The reducing-gas requirements are reported as equivalent to pure H_2 although, as mentioned, CO/H_2 mixtures can be used.

Waste Streams. No major waste streams are produced in the SCOT process (see Table 21). The most significant stream is the sour-water condensate obtained by cooling the tail gas in the direct contact heat exchanger prior to entry into the amine absorption column. This stream would amount to 0.44 to 0.63 l/sec and would be slightly acidic. It would be treated in a sour-water stripper for H_2S removal and then sent to the wastewater treatment system. The only other waste streams resulting from the process are degenerated amine solution from the amine regenerator and spent reduction catalysts. Both materials are encountered in normal refinery practice and should not constitute secondary sources of pollution.

Institute Francais du Petrole Processes (IFP)

Process Description. IFP has developed two Claus tail-gas-treatment processes, namely TGT-1500 (see Figure E-5) and TGT-150 (see Figure E-6).(49,50) The former process is capable of reducing the sulfur content in Claus tail gas down to about 3000 to 4000 ppm prior to incineration, while with the latter process, a reduction to 150 to 300 ppm is possible. The basic reaction involved in the TGT-1500 process is the same one that takes place in the reactors of a Claus unit:

$$2H_2S + SO_2 \xrightleftharpoons{\text{Cat}} 3S + 2H_2O \ .$$

Tail gas which exits a Claus unit at a temperature of about 265 to 285 F can be fed directly into the IFP reactor without cooling the gas. The reactor is essentially a packed column with a specially designed boot for collecting liquid sulfur. Mixed alkali metal salts of an organic acid(51) contained

TABLE 23. ESTIMATE OF UTILITIES REQUIREMENTS FOR SHELL CLAUS OFF-GAS TREATING UNIT (SCOT) APPLIED TO A 100-MT/D REFINERY CLAUS SULFUR PLANT(a)

Item	Value
Steam (3.40 atm, sat.), kg/hr	1,162(b)
Cooling Water (6.7 C rise), l/sec	82
Electricity, kWr/hr	140
Fuel Gas(c), scmm	1,224
Boiler Feed Water, l/sec	0.28
Chemicals(d)	
Reducing gas equivalent pure H_2, kg/hr	9.5
Operating Data	
Labor, men/shift	1/6-1/4
Maintenance, % FCI	2

(a) Taken from J. Wall Hydrocarbon Processing, 52(4), 114 (April, 1973).

(b) Net steam consumed in the process. Steam is produced following the reducing reactor (2,588 kg/hr) and consumed in the amine regenerator (3,750 kg/hr).

(c) Heating value of 9000 kg-cal/cu m.

(d) In addition, amine solution is used in the tail-gas scrubbing tower and reducing catalyst is used in the COS and CS_2 reduction reactor.

in a high-boiling polyglycol solvent serve to catalyze the reaction above the melting point of sulfur--generally in the range 120 to 130 C. The metal salts form a complex with H_2S and SO_2 in the feed gas, which in turn reacts with more of the two sulfur compounds to form elemental sulfur and regenerate the catalyst complex.(52) The sulfur coalesces and settles into the boot of the reactor, from which it is drawn as a molten product. In the reactor, the water of reaction is vaporized and carried out with the cleaned tail gas. To maintain the heat balance in the reactor, condensate is injected and vaporized together with the water of reaction. The solvent is generally a polyalkylene glcol, although alcohols, glycols, glycol ethers, or glycol polyethers may also be used.

One of the attractive features of the TGT-1500 process is that there is only one piece of rotating machinery in the unit--a centrifugal pump used to circulate the reaction solution. The only other equipment is a heat exchanger used in start-up, storage, and mixing and injection equipment used for catalyst and solvent makeup. The COS and CS_2 in the Claus tail gas are not converted in the IFP reactor, and will pass through untransformed to the incinerator. Recent Claus unit catalyst developments have made it possible to reduce the COS and CS_2 levels to 75-90 percent of their former values. However, this still remains a problem and the high sulfur content in the off-gas represents the major disadvantage of the IFP-1500 process.

To achieve better sulfur removal and treat COS and CS_2, IFP has developed the TGT-150 process. In this process, Claus tail gas is incinerated to convert COS, CS_2, H_2S, and elemental sulfur to SO_2. The hot flue gas then is cooled prior to an ammonium sulfite/bisulfite scrubber. In the cooling process, steam can be generated.

The flue gas containing sulfur oxides is introduced into a direct-contact cooling section of the absorber, where it is cooled further to 40 to 50 C by a downflowing stream of water. This sensible-heat-removal duty is small in relation to the heat of condensation of the water vapor in the saturated flue gas entering the absorber.

The flue gas leaving the direct contact cooling section of the absorber then enters a three-stage ammonia absorption section. Absorbent solution is essentially a mixture of aqueous ammonium sulfite and aqueous ammonium bisulfite having a pH between 5 and 7. The use of ammonium sulfite instead of ammonia as the absorbent minimizes the loss of ammonia to the atmosphere. The absorbent solution flows down through the tower countercurrent to the flue gas flow and the entire effluent is withdrawn from the bottom stage. The chemistry of ammonium sulfite/bisulfite absorption is identical to that presented for the sodium based system used in the Wellman-Lord system except for the ammonium cation (NH_4^+):

$$SO_2 + (NH_4)_2SO_3 + H_2O \rightleftarrows 2(NH_4)HSO_3 \,.$$

In the absorber ammonium sulfate is also found owing to reaction with oxygen

$$(NH_4)_2SO_3 + \frac{1}{2} O_2 \rightarrow (NH_4)_2 SO_4 \,.$$

An additional source of ammonium sulfate and thiosulfate is the disproportionation reaction:

$$6(NH_4)HSO_3 \rightarrow 2(NH_4)_2SO_4 + (NH_4)_2S_2O_3 + 2SO_2 + 3H_2O \,.$$

Since the flue gas exiting the absorber is about 40 to 50 C, it must be reheated prior to sending it to the stack. This usually is done by using a gas-fired reheater. Reheat usually is provided to give the plume buoyancy and protect the stack from corrosion due to condensation of moisture and acid gases.

The sulfitic brine leaving the absorber is heated and decomposed by a two-stage process into SO_2, NH_3, and H_2O. Although proprietary, the first-stage decomposer of the sulfitic brine is thought to be a submerged tube forced-circulation evaporator operated at a temperature of about 150 C and at low pressure. This type of apparatus usually consists of a heat exchanger fed by the circulation pump and a flash drum.

The concentrated solution from the flash drum is fed to the second stage, where the remaining ammonium sulfite and all of the ammonium sulfate and thiosulfate are decomposed. The liquid mixture is pumped through the furnace where the necessary heat is provided. Although there is some sulfur production during the decomposition of ammonium thiosulfate, the operating temperature of the decomposer would be chosen to prevent sulfur accumulation.

Stoichiometrically, the thermal decomposition proceeds as follows:

$$(NH_4)_2SO_3 \rightarrow 2NH_3 + H_2O + SO_2$$

$$NH_4HSO_3 \rightarrow NH_3 + H_2O + SO_2$$

$$(NH_4)_2S_2O_3 \rightarrow H_2O + 2NH_3 + S + SO_2 \ .$$

Reduction of the sulfates is by reaction with recycle hydrogen sulfide:

$$(NH_4)_2SO_4 + \frac{1}{3} H_2S \rightleftarrows \frac{4}{3} SO_2 + 2NH_3 + \frac{4}{3} H_2O \ .$$

The overhead gases from both the evaporator and the sulfate reduction furnace are then sent to an IFP catalytic reactor. This reactor is identical to that described previously for the TGT-1500 process. Operating temperatures are in the range from 120 to 130 C. An H_2S slip stream from the Claus plant feed is also fed to the bottom of the catalytic reactor along with the SO_2 stream to maintain the SO_2/H_2S at the optimum ratio required for efficient sulfur recovery in the reactor. Sulfur from the reactor is sent to a sulfur pit by a sulfur pump. Condensates and PEG solvent are mixed with the sulfur and must be recycled.

The vapor effluent off the IFP catalytic reactor consists principally of NH_3 and H_2O with traces of the PEG solution. Before it returns to the scrubbing section, this vapor is first cooled to the dew point temperature (about 100 C). The condensate and the ammonia solution are collected in a decanter. Ammonia solution, with makeup ammonia as NH_4OH, is then recycled to the absorber.

Ammonia volatility at high scrubbing-solution pH values will probably limit the SO_2 concentration in the process gas going to the reheater to a minimum level of 150 ppm. However, since a liquid-phase reaction is occurring, although uneconomic, theoretically the exit SO_2 concentration can be made to reach very low values. At 150 ppm SO_2, it is estimated that gaseous ammonia losses will be approximately 5 percent of the total ammonia fed to the top of the absorber. Some ammonia will also be destroyed during decomposition of the ammonium sulfate. This loss is expected to be less than 5 percent of the ammonia processed through the decomposer.

Commercial Status. The TGT-150 processes are licensed by the Institute Francais du Petrole. The TGT-1500 process is widely used and about 17 units have been built. Table 24 presents a partial list of TGT-1500 units.(53) Three plants are currently in operation in the United States on Claus plant tail gas. No information was obtained on available TGT-150 units, although three units are reported to be ready for start-up in Japan.(40)

Material Balance and Utilities. Sulfur-balance calculations for the TGT-1500 process are summarized in Tables 25 and 26. These calculations are based on information provided by IFP.(53) The basic assumptions used in making these estimates are:

(1) Removal of SO_2 and H_2S in the IFP reactor amounts to 90 percent of the input feed

(2) COS, CS_2, and sulfur vapor are not removed in the reactor.

For the design shown, the overall removal efficiency of the combined Claus-plant and TGT-1500 process would be only 98.5 percent. As mentioned previously, low sulfur recovery remains the major problem with the process.

An estimate of the utilities requirements for the TGT-1500 process is shown in Table 27.(53) Since the process involves few unit operations, the utility requirements are quite low. Unit values for the solvent and catalyst were not provided by IFP since they were proprietary. However, monetary values were provided by IFP and are reported in Table 27 in case operating costs need to be estimated.

Since the TGT-150 was not considered to be a commercial process in the sense that several units were operating, material balances and utility requirements were not estimated.

TABLE 24. LISTING OF ANNOUNCED TGT-1500 CLAUS-SULFUR-PLANT TAIL-GAS-PROCESSING UNITS

Company/Location	On-Stream Date	No. of Units/ Capacity, scmm	Number/Capacity of Claus Plants, MT/D
Nippon Petroleum Refining Company (Caltex)/Negishi, Japan	1971	1/493	1/300
Idemitsu Oil/ Himeji, Japan	1972	1/468	1/250
Showa Oil (Shell)/ Kawasaki, Japan	1972	1/99	1/80
Kyokuto Petroleum Industries (Mobil)/ Chiba, Japan	1972	1/336	1/200
Chevron Standard Ltd. (Chevron Research)/ Nevis, Alta., Canada	1972	1/448	1/260
Mitsubishi Oil Co. (Getty)/Mizushima, Japan	1972	1/392	1/180
Mitsubishi Oil Co. (Getty)/ Mizushima, Japan	1972	1/510	1/350
Phillips Petroleum/ Borger, Texas	1973	1/84	1/45
Ministry of Gas/ Orembourg I, USSR	1974	1/1344	1/800
Ministry of Gas/ Orembourg II, USSR	1974	1/1344	1/800
Ministry of Gas/ Orembourg III, USSR	1974	1/1344	1/800
Stauffer Chemical Co./ Delaware City, Del., USA	1973	Confidential	Confidential
Commonwealth Oil Refining/Ponce, Puerto Rico, USA	1973	1/105	1/60
Koa Oil No. 1/ Marifu, Japan	1973	--	--
Phillips/ Sweeny, Texas, USA	1973	1/84	1/4[illegible]
Koa Oil No. 2/ Marify, Japan	1974	--	--
Unannounced/	1975	--	1/400

TABLE 25. APPROXIMATE SULFUR BALANCE AND ESTIMATE OF WASTE STREAMS FOR TGT-1500 TAIL-GAS PROCESS

I. Basis

A. 100-MT/D Claus plant

B. 94 percent sulfur removal in Claus plant

C. 90 percent conversion of H_2S and SO_2 to S in tail gas

II. Sulfur Balance

A. Claus plant

Input - 104.471 MT/D
Recovered - 98.203 MT/D
Off-gas - 6.268 MT/D

B. TGT-1500 process

Input - 6.268 MT/D
Recovered - 5.275 MT/D
Off-Gas - 0.993 MT/D

III. Process Waste Streams

A. Intermittent contaminated water. With the new catalyst formulations, it takes about 2 years of operation before catalyst washing is necessary. At that time, about 28,000 liters of water would be required for washing the catalyst from a 100-MT/D Claus plant (about 151,400 liters from a 1,000-MT/D plant). The wash water would contain about 1 percent by weight of the organic solvent (polyalkylene glycol) and 20 to 25 percent by weight of the catalyst (mixed alkali metal salts of an organic acid). This waste stream would be treated in the refinery wastewater-treatment system or sent to the sewer system.

TABLE 26. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING A 100-MT/D REFINERY CLAUS PLANT PLUS THE IFP TGT-1500 TAIL-GAS PROCESS[(a)]

(Basis: Sulfur recovery in Claus unit of 94 percent)

	Claus Intake	Claus Exhaust	After Absorption Tower	After Incinerator
Composition, % vol.				
H_2S	89.9	0.85	0.085	--
SO_2	--	0.42	0.042	0.212%
S vapor and mist	--	0.05	0.050	--
COS	--	0.05	0.050	--
CS_2	--	0.04	0.075	--
CO	--	0.22	0.219	--
CO_2	4.6	2.37	2.376	4.483
HC (MW:30)	0.5	--	--	--
H_2	--	1.60	1.607	--
H_2O	5.0	33.10	33.990	30.502
N_2	--	61.30	61.545	64.299
O_2	--	--	--	0.504
Total	100.0	100.00	100.00	100.00
Temperature, C	40	140	119	650
Pressure, atm	1.45	1.26	1	1
Gas Quantity (Relative Amount), moles	1.00	3.00	2.83	4.03
Flow[(b)], scmm	56.78	170.35	160.72	228.98

(a) Material-balance data taken from letter to J. M. Genco, from J. W. Andrews, IFP (Dec. 21, 1973).

(b) Flow given in standard cubic meters per minute (scmm).

TABLE 27. ESTIMATE OF UTILITIES REQUIREMENTS FOR IFP TGT-1500 TAIL-GAS PROCESS APPLIED TO A 100-MT/D REFINERY CLAUS SULFUR PLANT(a)

Item	Value
Steam, kg/hr	(For start-up only)
Cooling Water, l/sec	(For shutdown only)
Electricity, kWhr/hr	35
Fuel Gas, scmh	0
Boiler Feed Water, l/sec	0
Chemicals	
Start-up solvent, $	18,500(b)
Solvent and catalyst consumption, $/year	10,500(b)
Condensate, l/sec	0.082
Operating Data	
Labor, men/shift	1/6-1/3
Maintenance, % FCI	5
Maintenance on catalyst, liters of water	28,000(c)

(a) Data taken from letter to Genco, J. M., from J. W. Andrews, IFP (Dec. 21, 1973).

(b) Unit values are proprietary.

(c) Maintenance on the catalyst once every 2 years. This is the value required for the wash water.

Waste Streams. There are no major waste streams generated by the TGT-1500 process. There are, however, intermittent contaminated wastewaters (see Table 25) that arise from washing the IFP reaction catalyst. With the new catalyst formulations, it takes about 2 years of operation before catalyst washing is necessary. At that time, about 28,000 liters of water would be required for washing the catalyst from an TGT-1500 process applied to a 100-MT/D Claus plant and about 151,400 liters from a 1,000-MT/D plant. The wash water would contain about 1 percent by weight of the organic solvent (polyalkylene glycol) and perhaps 20 to 25 percent by weight of the mixed alkali metal salts used as the catalyst. The waste stream would be treated in the refinery wastewater-treatment system or sent to an industrial sewer. While the solvent used in the TGT-1500 process is high boiling, its vapor pressure at reaction temperatures does cause some loss in the process off gas. The solvent is combusted to CO_2 and water in the incinerator, however, and thus should not represent a pollution problem of its own.

In addition to intermittent wastewaters generated in catalyst washing, a secondary source of pollution would arise in the case of the TGT-150 process. This involves the process off-gas leaving the top of the ammonia scrubber. Besides unreacted SO_2, the process gas will contain traces of NH_3 gas, entrained PEG solution, and sometimes a fine white particulate fume. The ammonia-SO_2 fume is thought to be the gas-phase reaction product between NH_3 and SO_2. It is a fine particulate fume which is highly visible and, because of its small size, difficult to remove from the gas. The fume forms over the scrubbing trays where appreciable NH_3 vapor pressure exists. A study currently is being conducted to determine the least expensive method of eliminating the fume.(50)

Chiyoda Thoroughbred 101 Process

Process Description. The Chiyoda Thoroughbred 101 process(54-56) is a wet flue-gas-desulfurization process which produces gypsum as an end product. Scaling and plugging problems in the scrubber are eliminated by scrubbing the tail gas with a dilute solution of sulfuric acid. The particular flow scheme applicable to tail gas treatment is shown in Figure E-7.

The incinerated off-gas from a Claus plant is cooled to about 55 C in a venturi saturator by means of a water spray in combination with an intercooler for heat rejection. Next the gas enters a countercurrent packed tower of grid-supported Tellerette packing where it is scrubbed with dilute H_2SO_4 to remove the SO_2. An oxidizing catalyst, ferric sulfate, and dissolved oxygen present in the scrubbing liquor increase the solubility of SO_2 in the dilute acid. The gas is then reheated by direct combustion of fuel and sent up the stack.

The recycle liquor from the bottom of the absorber is sent to an oxidizer where residual sulfurous acid is completely oxidized to sulfuric acid by air bubbles in the presence of the soluble ferric sulfate catalyst. Air is flown upward through the liquor at about five times the theoretical requirement. The net make of acid in the scrubber is bled from the oxidizer and neutralized with limestone in a crystallizer. The sulfuric acid tank between the oxidizer and the crystallizer has enough capacity to allow the absorber and the oxidizer to be drained for maintenance.

Limestone pulverized to 200 mesh has an apparent 100 percent utilization in the crystallizer. Pulverized limestone is conveyed to the crystallizer by an air stream. The $CaSO_4 \cdot 2H_2O$ (gypsum) crystals formed in the crystallizer are separated in a centrifuge and the dry solid is piled on the ground for storage or sold as product, while the mother liquor is recycled to the absorber. Catalyst makeup is added to the mother liquor tank and a purge stream from this tank is required to remove excess water and impurities, present in the limestone, from the system.

Clean process water is added to the system at the centrifuge in order to wash the gypsum product. Because the Claus plant tail gas contains about 33 percent water and the tail gas must be cooled, water condenses and must be removed from the system. Therefore, excess mother liquor in the form of a purge stream is pumped to the refinery wastewater treatment system in order to maintain a water balance on the tail gas desulfurization system.

The Chiyoda proces consists of three major reactions as follows:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (1)$$

$$H_2SO_3 + \frac{1}{2} O_2 \xrightarrow{catalyst} H_2SO_4 \qquad (2)$$

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \quad . \qquad (3)$$

Reaction (1) takes place in the absorber, Reaction (2) takes place mainly in the oxidizer, but also in the absorber, and Reaction (3) takes place in the crystallizer.

The SO_2-removal efficiency that can be obtained with the Chiyoda process is dependent upon the liquid-to-gas ratio (L/G) used in the absorber and the height of the packing in the absorber. Because the scrubbing liquor is dilute H_2SO_4, very high L/G's are required to obtain high removal efficiencies for SO_2. Roughly speaking, an L/G of about 54 l/cu m is required for 95 percent SO_2 removal at ordinary packing heights. Furthermore, for design reasons, the packing height in the absorber is limited to about 9 meters. For these reasons, the removal efficiency is limited to a maximum of about 95 percent, which means that the SO_2 content of the tail gas could be reduced from about 10,000 ppm to about 500 ppm. However, an SO_2 level of about 1,000 ppm in the treated tail gas is a more realistic expectation.

Commercial Status. The Thoroughbred 101 process was developed and is licensed by the Chiyoda Chemical Engineering & Construction Company, Ltd., of Yokohama, Japan. The process has been applied to tail gas from three refinery Claus plants and one combined industrial boiler-Claus tail-gas feed (see Table 28). However, since the process treats SO_2 rather than H_2S, it has found fairly wide acceptance in Japan as a flue-gas-desulfurization method on oil-fired boilers. In this regard, it has been applied to eight plants having industrial boilers as well as one industrial incinerator. Gas flow rates for the boiler application have ranged from 2,100 to 18,200 scmm while that for the incinerator is 434 scmm.

Material Balance and Utilities. Sulfur balance calculations are summarized in Table 29. Table 30 gives material-balance information for major gas streams in the process. These estimates are based in large part on information provided by Chiyoda.(55,56) The basic assumptions used in making these calculations are:

TABLE 28. LIST OF ANNOUNCED CHIYODA THOROUGHBRED 101 TAIL GAS PROCESSES UNITS FOR CLAUS SULFUR PLANTS

Company/Location	Startup Date	Unit/Capacity (SCFM)	Number/Capacity Claus Plants (LT/D)
Mizushima Refinery, Nippon Mining Co./Mizushima, Japan	November, 1972	1/20,800	1/200; 1/50
Sendai Refinery, Tohoku Oil Co./Sendai, Japan	February, 1973	1/8,800	1/90
Fuji Kosan Co., Ltd./ Kainan, Japan	November, 1972	1/98,000	(a)

(a) Combined industrial boiler and Claus sulfur plant incinerated tail gas.

TABLE 29. APPROXIMATE SULFUR BALANCE AND ESTIMATE OF WASTE STREAMS FOR THE CHIYODA THOROUGHBRED 101 FLUE-GAS-DESULFURIZATION PROCESS

I. Basis

- A. 100-M/D Claus plant
- B. 94 percent sulfur removal in Claus plant
- C. 92 percent sulfur removal in Chiyoda process

II. Sulfur Balance

A. Claus Plant

Input - 104.471 M/D
Recovered - 98.203 M/D
Off-gas - 6.268 M/D

B. Chiyoda Process

Input - 6.268 M/D
Recovered - 5.768 M/D
Off-gas - 0.4996 M/D

III. Waste Streams

A. By-Product Gypsum

(1) Rate = 35.3 MT/D

(2)

Composition	Wt %
H_2O	10.0
$CaSO_4 \cdot 2H_2O$	89.2
Impurities	
MgO (soluble)	0.2
Fe_2O_3	0.1
Insolubles	0.5
Total	100.0

(3) Treatment Method - This must either be sold or sent to a landfill.

B. Purge Stream

(1) Flow Rate = 0.148 l/sec

(2)

Composition	Wt %
H_2O	97.0
H_2SO_4	0.8
MgO	2.2
$Fe_2(SO_4)_3$	Trace
	100.0

(3) Treatment Method - Neutralized and sent to the refinery wastewater-treatment system or to an industrial sewer.

TABLE 30. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING 100-MT/D REFINERY CLAUS PLANT PLUS THE CHIYODA THOROUGHBRED 101 FLUE-GAS-DESULFURIZATION PROCESS

(Basis: Sulfur recovery in Claus unit of 94 percent)

	Claus Intake	Prior Incinerator	After Incinerator	After Cooling Section	After Absorber	After Reheater
Composition, & Vol.						
H_2S	89.9	.85	--	--	--	--
SO_2	--	.42	1.08	1.242	0.100	0.0865
S vapor and mist,	--	.05	--	--	--	--
COS	--	.05	--	--	--	--
CS_2	--	.04	--	--	--	--
CO	--	.22	--	--	--	--
CO_2	4.6	2.38	4.23	4.872	4.928	5.31
HC (MW: 30)	.5	--	--	--	--	--
H_2	--	1.60	--	--	--	--
H_2O	5.0	33.10	26.57	15.404	15.582	15.571
N_2	--	61.30	66.68	76.822	77.822	77.061
O_2	--	--	1.44	1.660	1.679	1.972
Total	100.00	100.00	100.00	100.00	100.00	100.00
Temperature, C	40	140	650	55	55	316
Pressure, atm	1.45	1.26	1	1	1	1
Gas Quantity (Relative Amount), moles	1.00	3.00	5.01	4.35	4.30	4.97
Flow[(a)], scmm	56.78	170.35	284.48	246.96	244	282.24

(a) Flow given in standard cubic meters per minute (scmm).

(1) Essentially complete conversion of all sulfur compounds to SO_2 in the incinerator prior to sending the tail gas to the Chiyoda process (fuel gas is 9,000 kg-cal/cu m with 10 percent excess air).

(2) 92 percent removal of SO_2 in the absorption column at an L/G ratio of 44 l/cu m.

(3) The off gas from the process is reheated to 316 F in a direct-fired reheater using 9,000 kg-cal/cu m fuel gas and 10 percent excess air.

(4) The acid produced is neutralized with limestone having the following composition (10 percent moisture and 90 percent solids):

Composition	Weight Percent (dry basis)
Fe_2O_3	0.20
MgO	1.86
CaO	53.40
CO_2	43.75
Other solubles	0.79
	100.00

(5) The MgO split between the purge stream and the product is 75 percent to 25 percent, respectively.

The Chiyoda process should be capable of reducing the sulfur level in the off gas to about the 1,000 ppm. Further sulfur reductions are possible but would result in inordinately high liquid-to-gas recirculation rates in the absorber. Overall sulfur recovery in the Claus plant with tail-gas treatment is estimated to be about 99.5 percent. An estimate of the utilities required for a unit treating the tail gas from a 100-MT/D Claus plant is given in Table 31.

Waste Streams. The waste streams produced by the Chiyoda process include a solid product gypsum with a moisture content of 5 to [illegible] percent and a mother liquor purge stream (see Table 29). The purity of the product

TABLE 31. ESTIMATE OF UTILITY REQUIREMENTS FOR CHIYODA THOROUGHBRED 101 TAIL-GAS PROCESS FOR 100-MT/D REFINERY CLAUS SULFUR PLANT

	Value
Steam (32 atm, sat), kg/hr	2,470$^{(a)}$
Cooling Water (10 C rise), l/sec	64.5
Electricity, kwh/hr	425
Fuel Gas,$^{(b)}$ scmm	4,256
Boiler Feed Water, l/sec	0.871
Chemicals	
Limestone, MT/D	21.1$^{(c)}$
Operating Data	
Labor, men/shift	1/3
Maintenance, percent FCI	5

(a) Steam generated in the process.

(b) Heating value of 9,000 kg-cal/cu m.

(c) Wet basis at 10 percent water and 90 percent solids.

gypsum is dependent upon the level of dilute-acid-insoluble impurities in the limestone feed. The soluble impurities washed out of the gypsum, by adding process water at the centrifuge, end up in the purge stream. The gypsum produced can be of sufficient quality to permit its use in wallboard. If the gypsum could not be sold, it would have to be sent to a landfill for final disposal.

The mother-liquor purge stream consists of dilute sulfuric acid (about 1 weight percent), soluble impurities (mainly $MgSO_4$) from the limestone, and a small amount of dissolved catalyst (about 2,000 ppm of Fe^{+3}). It would normally be neutralized and sent to the refinery wastewater-treatment system or, alternatively, to an industrial sewer.

Sulfreen Process

Process Description. The Sulfreen process(48,57-59) (see Figure E-8) was jointly developed by Lurgi Apparate-Technik, Frankfurt, West Germany, and the Societe Nationale des Petroles d' Aquitaine (SNPA), Lacq, France. This process reduces the sulfur content in Claus-plant tail gas by further promoting the Claus reaction on a catalytic surface in a gas/solid batch reactor:

$$2H_2S + SO_2 \overset{\text{cat.}}{\rightleftarrows} 3S + 2H_2O.$$

The Claus-plant tail gas is first countercurrently contacted with liquid sulfur to wash out any sulfur particles that may have been entrained in the sulfur plant.

The tail gas then is introduced to a battery of reactors (six shown) where the Claus reactions are carried out at lower temperatures (127 to 149 C) than those utilized in the sulfur plant. The purpose of the reduced temperature is to take advantage of the more favorable equilibrium conditions of the Claus reaction which is reversible. The catalyst is usually activated carbon, although alumina is also used.

For desorption of sulfur from loaded beds, a regeneration gas consisting essentially of nitrogen is used. The nitrogen is heated in several steps up to 500 C in a gas-fired heater and then cycled through the activated carbon bed from top to bottom. The temperature is kept below 300 C until all carbon dioxide and water are displaced from the beds. Otherwise, carbon losses would occur through gasification.

For the desorption of sulfur, the temperature is raised to 400 C. Sulfur vaporizes and is swept away with the nitrogen; most of it is precipitated in the condenser ahead of the sulfur washing tower. The washer itself further reduces the level of elemental sulfur down to 140 mg/cu m. At the same time, the regeneration gas is cooled in these two units to approximately 120 C. The heat released in the condenser produces saturated steam of 5.76 atm from boiler feedwater, and it is used for such tasks as heating the molten sulfur product.

The process reduces entrained sulfur to a minimum as the catalyst acts as a very effective adsorbent for liquid sulfur. A Sulfreen unit may consist of as little as three reactors, two in adsorption and one in desorption service. The number of reactors is determined mainly by economic considerations and the degree of sulfur (H_2S and SO_2) removal desired. In the process, COS and CS_2 are not affected and this is a major disadvantage of the process. Since only solid adsorbents are used, no liquids except sulfur condense, and the process is free of major liquid disposal problems. This is the main advantage of the Sulfreen process.

A one-stage Sulfreen process, similar to that shown in Figure E-8, is capable of reducing the tail-gas sulfur level by about 80 to 85 percent for sulfur mist, SO_2 and H_2S. A second-stage option has been considered to further reduce the sulfur content. In the second stage, the tail gas is injected with air and sent to another catalytic bed in which hydrogen sulfide is oxidized directly to sulfur. Currently, the second stage is not commercially available. It is claimed that the outlet H_2S concentration from the second stage can be reduced to 10 ppm.(57) This is highly unlikely and would require a second-stage efficiency of 99.5 percent. A more realistic second-stage efficiency would be 85 to 95 percent, which would bring the total sulfur level in the process gas going to the incinerator down to 100 to 400 ppmv equivalent H_2S.

Commercial Status. The Sulfreen process is licensed by Lurgi Apparate-Technik, Frankfurt, West Germany, Societe Nationale des Petroles d'Aquitaine, Lacq, France, and by the R. M. Parsons Company, Los Angeles, California. Three commercial-scale plants are already on-stream (see Table 32). The first, in Lacq, France, handles approximately 3.2 million standard cubic meters per day (scmd) of gas and employs six reactors, three of which contain activated carbon while the others contain alumina.(57) The second and third units in Ram River, Alberta, Canada, were started up in the spring and fall of 1972, respectively. The Ram River units recover sulfur as product from tail gases off four 1,000 MT/D Claus sulfur units. These Sulfreen units are rated at about 11.2 million scmd total. In these two units, all reactors used only activated carbon.(58) In addition to these operating units, four other large-scale plants treating a total of approximately 19.6 million scmd are under construction.

Material Balance and Utilities. Sulfur-balance calculations for a Sulfreen unit handling the tail gas from a 100-MT/D Claus plant are summarized in Table 33. The sulfur-balance values were based on the material balance information presented in Table 34. Only that portion of the process undergoing adsorption was considered in making material-balance calculations. The basic assumptions used in arriving at the information shown in Tables 33 and 34 are:

(1) The adsorption reactors are operated essentially at the same temperature as the tail gas exiting the Claus plant (140 C).

(2) The sulfur wash prior to the reactors removes 75 percent of the entrained sulfur mist entering the washer.

(3) The gas-phase SO_2 and H_2S concentrations are reduced by 80 percent in the reactors.

(4) COS and CS_2 are not appreciably removed in the process.

(5) The off gas from the reactors is incinerated in the Claus-plant incinerator using 9,000 kg-cal/cu m fuel gas and 10 percent excess air.

TABLE 32. PARTIAL LIST OF ANNOUNCED SULFREEN TAIL-GAS-PROCESSING UNITS FOR CLAUS SULFUR PLANTS[a]

Company/Location	Start-up Date	Capacity, scmm	Number/Capacity of Claus Plants, MT/D
SNPA/France Lacq Nat. Gas Plant	1970	11,952	1/114
Aquitaine Co. (Canada) Ltd.)/Alberta, Canada Ram River Gas Plant	1972	--	2/400

(a) Four other units are thought to be under construction.

TABLE 33. APPROXIMATE SULFUR BALANCE AND WASTE STREAMS FOR SULFREEN TAIL-GAS PROCESS

I. Basis

A. 100-MT/D Claus plant

B. 94 percent sulfur removal in Claus plant

C. 75 percent sulfur mist (S_8) removal in sulfur washing unit and approximately 80 percent sulfur (H_2S, SO_2) removal in one-stage Sulfreen unit(a)

II. Sulfur Balance

A. Claus Plant

Input - 104.471 MT/D
Recovered - 98.203 MT/D
Off gas - 6.268 MT/D

B. Sulfreen Process

Input - 6.268 MT/D
Recovered - 4.536 MT/D
Off gas - 1.732 MT/D

III. Waste Streams

None

(a) 80 percent removal is approximate since SO_2 and H_2S in the inlet feed are not quite in stoichiometric ratio.

TABLE 34. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING 100MT/D REFINERY CLAUS PLANT PLUS THE SULFREEN TAIL-GAS PROCESS

(Basis: Sulfur recovery in Claus unit of 94 percent)

	Claus Intake	Claus Exhaust Prior Incinerator	After Sulfur Wash	Off-Gas	After Incinerator
Composition(a)					
H_2S	89.9	0.85	0.850	0.180	--
SO_2	--	0.42	0.420	0.085	3,385 ppm
S vapor and mist	--	0.05	0.013	0.013	--
COS	--	0.05	0.050	0.051	--
CS_2	--	0.04	0.040	0.040	--
CO	--	0.22	0.220	0.222	--
CO_2	4.6	2.37	2.370	2.39	2.9
HC (MW:30)	0.5	--	--	--	--
H_2	--	1.60	1.6	1.62	--
H_2O	5.0	33.10	33.1	33.44	28.93
N_2	--	61.30	61.3	61.93	67.23
O_2	--	--	--	--	0.61
Total	100.00	100.00	100	100	100.0
Temperature, C	40	140	140	140	650
Pressure, atm	1.45	1.26	18.5	1	1
Gas Quantity (Relative Amount), moles	1.00	3.00	3.00	2.97	4.40
Flow(b), scmm	56.78	170.35	170.32	168.62	250.04

(a) Percent by volume unless otherwise noted.

(b) Flow given in standard cubic meters per minute (scmm).

Under this set of assumptions, the overall sulfur-removal efficiency (Claus plant plus Sulfreen process) would be about 98.3 percent. The sulfur concentration in the Sulfreen process off gas calculated as H_2S prior to incineration would be about 5000 ppm. Utilities requirements for the Sulfreen process are shown in Table 35. These data were scaled down to the size required for a 100-MT/D Claus unit from information presented in Krill and Stopp(57) and Wall(48).

Waste Streams. Since only solid adsorbents are used, no liquids except sulfur condense, and the process is free of major liquid-disposal problems. The catalyst (activated carbon or activated alumina) life expected is about 4 years, but it would have to be disposed of or regenerated at that time. These streams should present no major problems since both types of waste (degenerated catalyst and sulfur-contaminated water) are often encountered in refinery practice.

ESTIMATION OF NATIONWIDE REFINERY SULFUR PLANT EMISSIONS IN 1975

Emissions of sulfur from petroleum refineries are a complex function of the sulfur content of the crude oil being processed, the complexity of the refinery, and its energy balance. Sulfur enters the refinery in the oil, in any purchased fuel oil or gas, and as sulfuric acid purchased for process use. A large part of this sulfur routinely leaves the refinery in the various products, as spent sulfuric acid shipped out for regeneration and as sulfides or sulfates in waste liquids, or is recovered as a by-product in sulfur-recovery plants. The balance is emitted to the atmosphere mainly as sulfur dioxide, although some SO_3 and H_2S may also be released. These sulfur emissions occur mainly during fuel-gas-burning operations in process heaters and boilers and to a lesser extent as tail gas from Claus sulfur plants. In this section of the report, nationwide sulfur emissions from refinery Claus plants are estimated for the year 1975.

To estimate nationwide refinery Claus plant emissions, several assumptions are required:

TABLE 35. ESTIMATE OF UTILITIES REQUIREMENTS FOR SULFREEN PROCESS ADDED TO 100-MT/D REFINERY CLAUS SULFUR PLANT

	Alumina Catalyst	Activated Carbon Catalyst
Steam (4.76, sat), kg/hr	735[(a)]	785[(a)]
Cooling Water, l/sec	Nominal	Nominal
Electricity, kwh/hr	124	69
Fuel Gas, scmh	60.9	65.0
Boiler Feed Water, l/sec	0.189	0.221
Chemicals		
Nitrogen, scmh	44.9	44.9
Catalyst, kg/hr	11.0	5.6
Operating Data		
Labor, men/shift	1/3-1/2	1/3-1/2
Maintenance, percent FCI	3.3	3.3

(a) Steam produced in process.

(1) The nationwide average physical properties of petroleum are
    (a) Specific gravity = 0.876(60)
    (b) Sulfur content = 0.92 percent.

(2) The average capacity factor of refinery Claus plants is about 66 percent.(60)

(3) Sulfur recovery from existing tail-gas units at refineries was negligible in 1973.

(4) The average capacity factor for petroleum refineries in 1973 was about 95.7 percent.(61)

(5) Additional refining capacity between 1973 and 1975 will process high-sulfur oil (i.e., about 2 percent sulfur).

(6) On the average, Claus sulfur plants in refineries are about 92 percent efficient, i.e., an average plant will recover on a molar basis about 92 percent of the input H_2S as elemental sulfur.

(7) Tail gas processes are, on the average, about 94 percent efficient and thus will raise the overall level of sulfur recovery (Claus plant plus tail-gas process) to about 99.5 percent, and this represents best available technology.

(8) Current refinery sulfur-recovery capacity can be obtained from the data of Beers(11) and amounted to 7,999 MT/D (see Tables 5 and 6) in 1973.

Domestic refining capacity in place as of April, 1973, is shown in Table 6. Announced additional refining capacity scheduled for start-up prior to January 1, 1975, is shown in Table 36.(20) On the basis of these data, domestic refining capacity will increase by about 1 percent between 1973 and 1975, i.e., from about 1.836×10^6 MT/D to 1.854×10^6 MT/D in 1975. Likewise, the national average sulfur content of the crude oil being processed will increase from about 0.92 to 0.93 percent over this 2-year period. Consequently, refinery Claus-sulfur-plant capacity in 1975 can be estimated from the 1973 value as:

$$\text{1975 Claus capacity} = 7{,}999 \text{ MT/D} \times 1.01 \times (0.93/0.92) = 8{,}167 \text{ MT/D}.$$

TABLE 36. STATE-BY-STATE LISTING OF ANNOUNCED ADDITIONAL REFINERY CAPACITY BY 1975(20)

State/Company/City, County	Start-up Date	Refinery Capacity,[a] 10^3 metric tons/day
Pennsylvania		
ARCO		
Philadelphia	Late 1973	3.4
California		
ARCO		
Carson	Late 1973	2.7
Illinois		
Clark		
Hartford	Late 1974	6.2
Kansas		
ARCO		
Arkansas City	Late 1974	2.7
Texas		
Howell		
Corpus Christi	Early 1974	2.7
New Mexico		
Navajo		
Artesia	May, 1974	0.8
	TOTAL	18.5

(a) Based upon 7.31 barrels of oil per metric ton.

Sulfur emitted in tail gas can be estimated from the capacity factor (2/3) and the approximate percentage sulfur recovery in Claus plants (92 percent), i.e., 1975 tail-gas emissions (MT sulfur/yr = (8,167 MT/D) x (2/3) x (365 days/yr)(0.08/0.92) = 0.173 x 10^6 MT/yr. This value should be corrected for sulfur recovery in tail-gas processing which will occur in 1975. The data given in Tables 10, 14, 16, and 20 suggest that approximately 1,854 MT/D of Claus plant capacity will be equipped with tail-gas processing by 1975. This translates into approximately 0.037 x 10^6 MT/yr of sulfur being recovered from tail-gas processing, i.e., MT/yr = (1,854 MT/D)(2/3)(365)(0.08/0.92)(0.94) = 0.037 x 10^6 MT/yr. Thus, correcting the uncontrolled emissions number (0.173 x 10^6 MT/yr), one obtains the estimate for 1975 sulfur emissions from refinery Claus plants;

1975 tail-gas emissions (MT sulfur/yr) = (0.173 - 0.037) x 10^6 = 0.136 x 10^6 MT/yr,

or in terms of SO_2 emitted

1975 tail-gas emissions (MT SO_2/yr) = (0.136 x 10^6) x 2 = 0.272 x 10^6 MT/yr.

It is interesting to compare the estimate of uncontrolled emission of SO_2 from refinery sulfur plants to other sources in 1975. Table 37 summarizes estimated nationwide SO_2 emissions without abatement from several sources. The estimates shown in Table 37 were made in 1970 by the National Research Council's Ad Hoc Panel on Control of SO_2 from Stationary Combustion Sources. By far the major emitter of SO_2 would be fossil-fuel fired power plants. By way of comparison with major sources, refinery Claus sulfur-plant emissions are rather small, i.e., about 0.3 x 10^6 MT/yr out of a total of 43.7 x 10^6 MT/yr.

TABLE 37. ESTIMATED ANNUAL SULFUR DIOXIDE EMISSIONS IN THE UNITED STATES IN 1975--NO ABATEMENT[(a)]

	10^6 Metric Tons/Year
Power Plant Operations (Coal and Oil)	27.3
Other Combustion of Coal	3.9
Combustion of Petroleum Products (Excluding Power Plant Oil)	3.3
Smelting of Metallic Ores	4.2
Petroleum Refinery Operations	2.9
Miscellaneous Sources	2.1
TOTAL	43.7

(a) Data taken from "Abatement of Sulfur Oxide Emissions from Stationary Combustion Sources", National Research Council, COPAC-2, Washington, D.C. (1970).

CONCLUSIONS

On the basis of the foregoing analyses and review of sulfur recovery at petroleum refineries, several conclusions can be drawn:

(1) Petroleum refineries differ widely and generalizations about sulfur recovery and emissions are difficult to make.

(2) Sulfur occurs in petroleum processing in the form of four types of compounds; hydrogen sulfide and mercaptans, elemental sulfur, carbonyl sulfide (COS), and carbon disulphide (CS_2), and neutral sulfur compounds.

(3) Emissions of sulfur to the atmosphere at petroleum refineries occur mainly as SO_2 from process heaters, boilers, and flares, in the tail gas from sulfur-recovery plants, and as trace amounts of H_2S that escape during routine processing operations.

(4) Virtually all sulfur currently being recovered at petroleum refineries is done by vapor-phase oxidation of H_2S in straight-through Claus plants. Domestic sulfur recovery capacity found at refineries amounts to about 8,000 MT/D. Plants are normally operated at two-thirds of capacity and sulfur-recovery efficiencies of 90 to 95 percent. Acid-gas-feed sources to refinery Claus plants originate mainly from sour-water strippers and amine regenerators associated with hydrocracking units, hydrotreating units, and fuel-gas desulfurization operations.

(5) Fuel-gas desulfurization using amines and other reactive liquids, as well as sulfur recovery in Claus plants, is well-established technology. Both technologies are commercially available and have been practiced in the petroleum industry for many years.

(6) An alternative to Claus-plant technology is sulfur recovery by way of liquid-phase oxidation of H_2S. Good

examples of this technique would be the Stretford or Giammarco-Vetrocoke processes, which use multiple, coupled redox reactions in solution to produce elemental sulfur. Such processes have been used in the European natural-gas industry and are now being introduced into the U.S. The Stretford process is currently being used for fuel-gas desulfurization and also is incorporated into the Beavon and Cleanair tail-gas-treatment processes.

(7) Processing of tail gases from Claus plants found at refineries (also natural-gas plants) would be considered emerging technology and is only now beginning to be practiced in the U.S. The leading U.S. processes are the Beavon, SCOT, Wellman-Lord, IFP-TGT-1500 process, and Cleanair processes. In addition, the Chiyoda Thoroughbred 101 and Sulfreen are promising processes that have not yet been tried on domestic refinery Claus plants. All but the Chiyoda process recover elemental sulfur. Approximately 964 MT/D of parent-Claus-plant capacity has been equipped with tail-gas processing. These plants are now mainly in start-up difficulties. An additional 890 MT/D of parent-sulfur-plant capacity is due to be equipped (announced plants) in the U.S. by 1975.

(8) By use of tail-gas processing, overall sulfur recovery can be increased to greater than 99 percent of the total input sulfur to the Claus plant. The utilities required and waste streams generated by the operation of tail-gas processing are not inordinate. Roughly, the utilities (hence, operating cost) are of the same order as those involved in the parent sulfur plant. Waste streams in the aqueous-based processes usually involve either a sour-water or acid-water purge stream resulting from condensation of water in the tail gas. Depending upon the process, this water is usually sent

to either the sour-water stripper for H_2S removal or to the refinery wastewater-treatment system for neutralization. In addition, several processes, i.e., the Beavon, Cleanair, and Wellman-Lord, have purge streams containing metal salts that must be disposed of. Currently, they are being discharged to industrial sewer systems. Their small size does not appear to cause major problems. Also, the process licensors are developing techniques for on-site treatment.(15)

(9) Nationwide sulfur emissions from refinery Claus plants were estimated to be approximately 0.136×10^6 MT/yr (0.272×10^6 MT of SO_2) in 1975. In comparison with other emission sources of sulfur, refinery Claus-plant emissions appear to be quite small, i.e., it is estimated that less than 1 percent of the 1975 unabated SO_2 sources would be attributable to refinery Claus-plant tail gas.

REFERENCES

(1) Stern, A. C., Air Pollution, 2nd Edition, Vol III, Academic Press, New York, N. Y. (1968), pp 101-103.

(2) Updegraff, N. C., and Reed, R. M., The Petroleum Engineer, 26 (10), C57-C63 (September, 1954).

(3) Blake, R. J., Oil & Gas Journal, 65 (2), 102-108 (January 9, 1967).

(4) Fitzgerald, K. J., and Richardson, J. A., Hydrocarbon Processing, 45 (7), 125-129 (July, 1966).

(5) Klein, J. P., Oil and Gas International, 10 (9), 109-112 (September, 1970).

(6) Kohl, A. L., Petroleum Processing, 6 (1), 26-31 (1951).

(7) Holder, H. L., Oil & Gas Journal, 64 (18), 83-86 (May 2, 1966).

(8) Beychok, M. R., Aqueous Wastes From Petroleum and Petrochemical Plants, John Wiley and Sons, New York, (1967).

(9) Anonymous, Manual on Disposal of Refinery Wastes, Vol I. Wastewater Containing Oil, Vol III, Chemical Wastes, Vol IV. Sampling and Analysis of Wastewater, American Petroleum Institute, Washington, D.C. (1969).

(10) Armstrong, T. A., Oil & Gas J., 66 (25), 96-98 (June 17, 1968).

(11) Beers, W. D., "Characterization of Claus Plant Emissions", Final Report from Process Research, Inc., to the United States EPA, Contract No. 68-02-0242, Task No. 2, Report No. EPA-R2-73-188 (April, 1973).

(12) Maddox, R. N., and Burns, M. D., Oil & Gas J., 66 (37), 130-133 (September 9, 1968).

(13) Grekel, H., Kunkel, L. V., and McGalliard, R., Chemical Engineering Progress, 61 (9), 70-73 (1965).

(14) Grekel, H., et al, Oil & Gas J., 59 (23), 80-81 (June 5, 1961).

(15) Goar, B. G., Hydrocarbon Processing, 47 (9), 248-252 (1968).

(16) Grekel, H., and Kilmer, J. W., Oil & J., 66 (44), 88, 93-101 (October 28, 1968).

(17) Townsend, F. M., and Reid, L. S., Petroleum Refiner, 37 (11), 263-266 (1958).

(18) Chute, A. E., Trans. AIME, 241, 314-318 (1968).

(19) Anonymous, Engineering and Mining Journal, 169 (10), 85-92 (October, 1968).

(20) Anonymous, Oil & Gas J., 71 (32), 32-33 (August 6, 1973).

REFERENCES
(Continued)

(21) Nader, J. E., Wesselingh, J. A., and Groenendaal, W., "The Shell Off-Gas Treating Process", paper presented at the 74th National Meeting of the AIChE, New Orleans, Louisiana, March 11-15, 1973.

(22) Ellwood, P., Chem. Eng., 71 (15), 128-130 (July 20, 1964).

(23) Hasbe, N., Tokyo Gas Co. Ltd, Research Report (no date given).

(24) Beavon, D. K., and Vaell, R. P., paper presented at the 37th Mid-Year Meeting of the API's Division of Refining, New York, N. Y., May 8-11, 1972.

(25) Beavon, K. D., Chem. Eng., 78, 71-73 (December 13, 1971).

(26) Thomas, G.L., and Plum, E., paper presented at the 71st National AIChE Meeting, Dallas, Texas, February 20-23, 1972.

(27) Goar, B. G., Hydrocarbon Processing, 47 (9), 72 (1968).

(28) Jennett, E., Oil & Gas J., 60 (18), 72 (April 30, 1962).

(29) Swain, C. D., Jr., Hydrocarbon Processing, 49 (3), 127 (1970).

(30) Kohl, A. L., and Riesenfeld, F. C., Chem. Eng., 66 (12), 127-128 (June 15, 1959).

(31) Anonymous, Oil & Gas J., 69 (50), 39 (December 13, 1971).

(32) Ellwood, P., Chem. Eng., 71 (15), 128-130 (July 20, 1964).

(33) Anonymous, Oil & Gas J., 69 (41), 68-69 (October 11, 1971).

(34) Anonymous, Hydrocarbon Processing, 50, 119 (April, 1971).

(35) Sedman, C., private communication, EPA, Durham, North Carolina (December, 1973).

(36) Mitachi, K., Chemical Engineering, 80 (21), 78-79 (October 15, 1973).

(37) Maddox, R. N., and Burns, M. D., Oil & Gas J., 66 (23), 90-95 (June 3, 1968).

(38) Jennett, E., Oil & Gas J., 60, 72-77 (April 30, 1962).

(39) Meuly, W. C., "Cataban Process for the Removal of Hydrogen Sulfide from Gaseous and Liquid Streams", paper presented at the 12th Annual Purdue Air Quality Conference, Purdue University, West Lafayette, Indiana (November, 7-8, 1973).

REFERENCES
(Continued)

(40) Anonymous, "Present Technology for Sulfur Recovery--Status Report for the Florida Department of Pollution Control", Report from Walk, Haydel & Associates, Inc., WH&A Job No. 72-1634 (May 31, 1973).

(41) Davis, J. C., Chem. Eng., 78, 43-45 (November 29, 1971).

(42) Anonymous, Oil & Gas J., 70 (6), 65 (February 7, 1972).

(43) Wall, J., Hydrocarbon Processing, 52 (4), 116 (April, 1973).

(44) Private communication, letter to J. M. Genco, from C. B. Earl, Davy Powergas Inc., Lakeland, Florida (December 13, 1973).

(45) Groenendaal, W., Nv., M., and Van Meurs, H. C., Petro. & Petrochem. Int., 12 (9), 54-58 (1972).

(46) Dautzenberg, F. M., Nader, J. E., and Van Ginneken, A.J.J., Chemical Engineering Progress, 67 (8), 86-91 (1971).

(47) Private Communication, letter to J. M. Genco from E. G.Foster, Shell Development Corporation, Houston, Texas (January 22, 1974).

Wall, J., Hydrocarbon Processing, 52 (4), 115 (April, 1973).

(49) Anonymous, Hydrocarbon Processing, 50 (5), 89-91 (May, 1971).

(50) Newcombe, G. M., Maxwell, M. A., and Rochelle, G. T., "Control of Sulfur Dioxide Emission from Stack Gases -- Discussion of Promising Soluble Base Aqueous Scrubbing Processes", paperpresented at the 17th Annual AIChE Meeting, Delaware Valley Section, Philadelphia, Pennsylvania, March 21, 1972.

(51) Hirai, M., Odello, R., and Shimamura, H., Chem. Eng., 79, 78-79 (April 17, 1972).

(52) Barthel, Y., Deschamps, A., Frankowiak, S. and Andrews, J. W., "IFP Processes for Recovering H_2S and SO_2 from Claus Unit Tail Gas and for Cleaning SO_2 from Stack Gas", paper presented at the 66th Annual Meeting of the Air Pollution Control Association, Chicago, Illinois, June 24-28, 1973.

(53) Private communication, letter to J. M. Genco from J. W. Andrews, Institute Francais du Petrole, New York, N. Y., (December 21, 1973).

(54) Anonymous, "Report of the Edison Electric Institute Study Program on SO_2 Removal Processes in Japanese Plants", Edison Electric Institute, New York, N. Y. (1973).

(55) Private communication, letter to J. M. Genco from T. Kamada, Chiyoda Chemical Engineering & Construction Co., Ltd., Yokohama, Japan (January 9, 1973).

REFERENCES
(Continued)

(56) Idemura, H., "New Flue Gas Desulfurization Process", report by the Chiyoda Chemical Engineering & Construction Co., Ltd., Yokohama, Japan (June 20, 1973).

(57) Krill, N., and Storp, K., Chem. Eng., 80 (17), 84-85 (July 23, 1973).

(58) Anonymous, Oil & Gas J., 70 (26), 85-88 (June 26, 1972).

(59) Farrar, G. L., Oil & Gas J., 68 (42), 72-75 (October 19, 1970).

(60) Hobson, G. D., and Pohl, W., Modern Petroleum Technology, 4th Edition, John Wiley & Sons, New York, N. Y. (1973), p 209.

(61) Cantrell, A., Oil & Gas J., 71 (14), 99-121 (April 2, 1973).

APPENDIX A

FLOW DIAGRAMS FOR FUEL-GAS-DESULFURIZATION PROCESSES

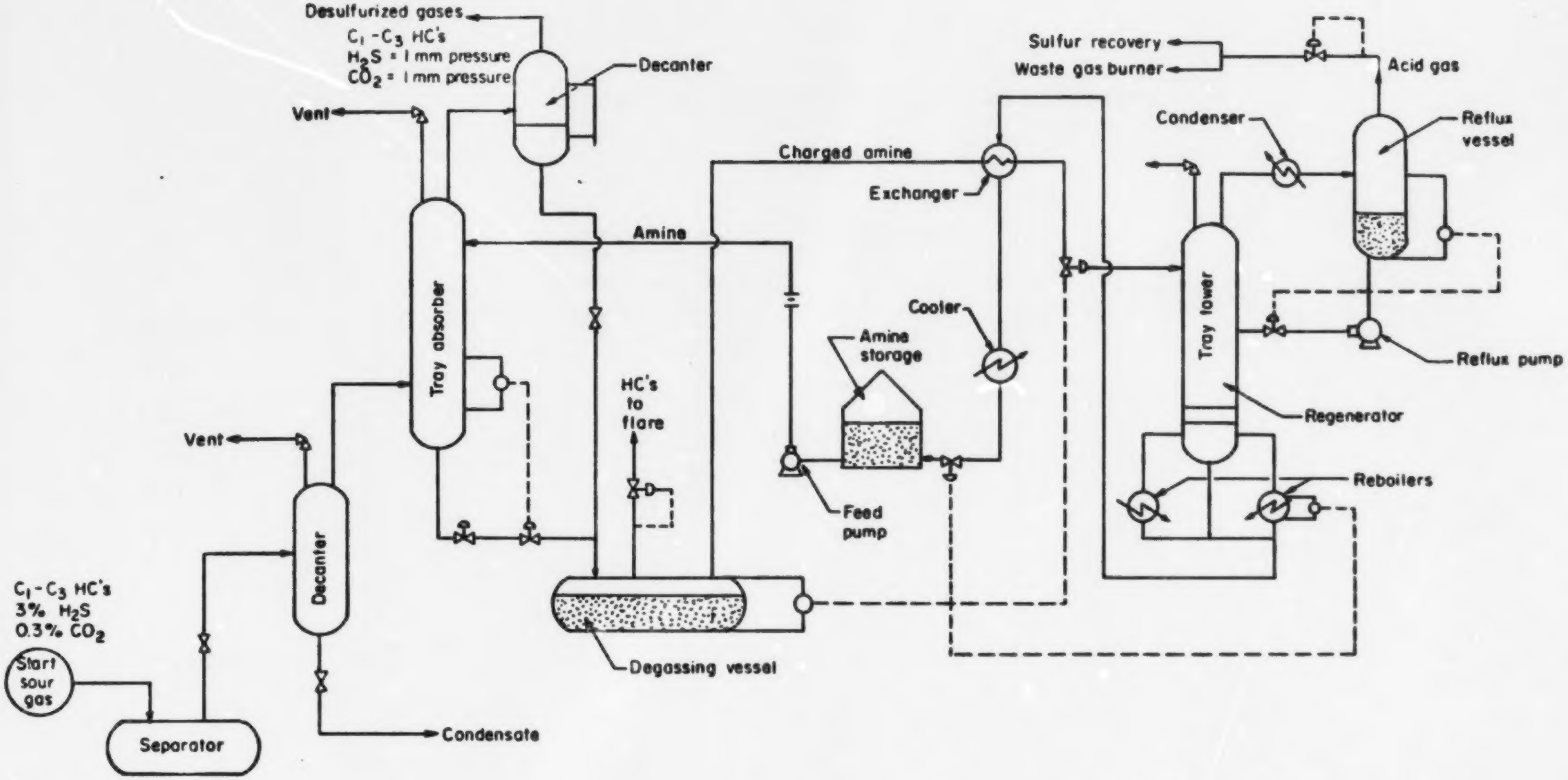

Desulfurized gases
C_1 - C_3 HC's
H_2S = 1 mm pressure
CO_2 = 1 mm pressure
Decanter
Vent
Vent
Tray absorber
Amine
Charged amine
Exchanger
Cooler
Amine storage
Feed pump
HC's to flare
Degassing vessel
Decanter
Condensate
Separator
C_1-C_3 HC's
3% H_2S
0.3% CO_2
Start sour gas
Sulfur recovery
Waste gas burner
Acid gas
Condenser
Reflux vessel
Tray tower
Reflux pump
Regenerator
Reboilers

FIGURE A-1. FLOW DIAGRAM FOR H_2S REMOVAL BY AMINE SOLUTION (GIRBOTOL PROCESS)

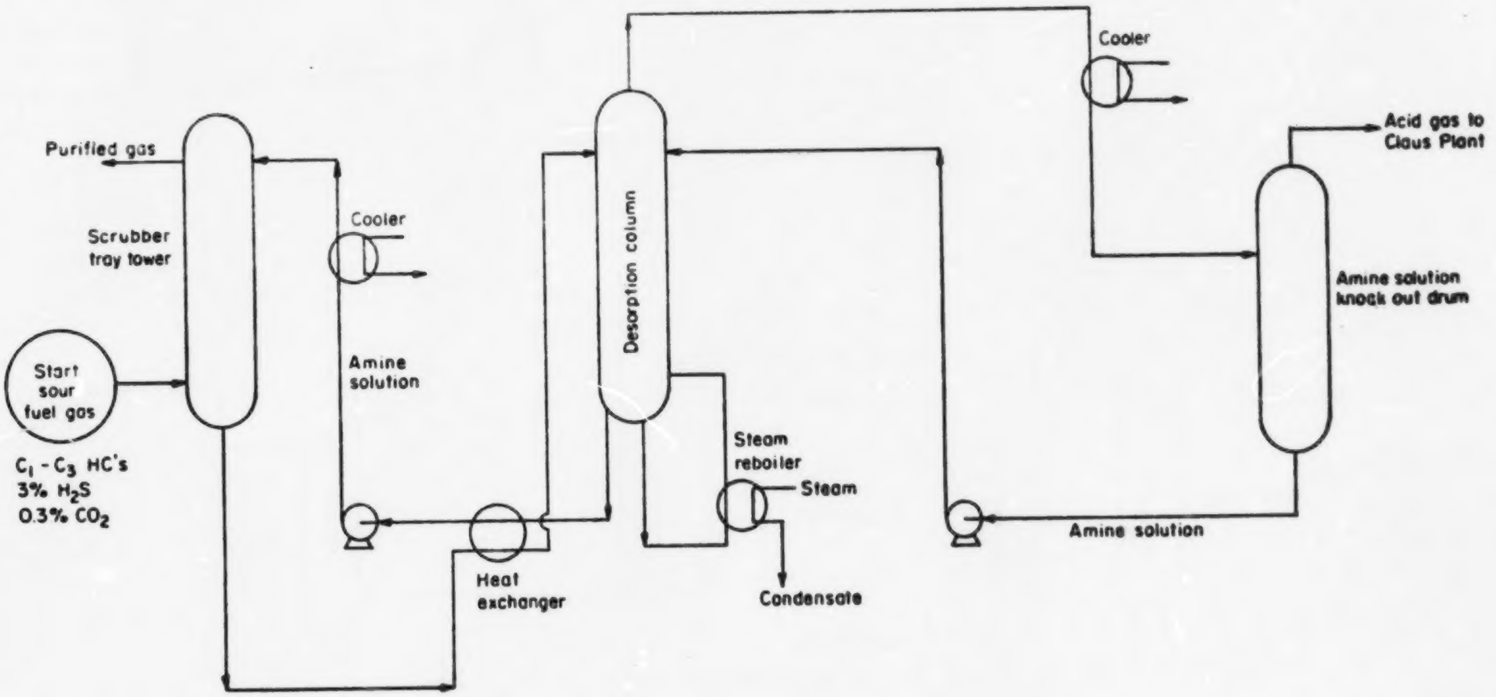
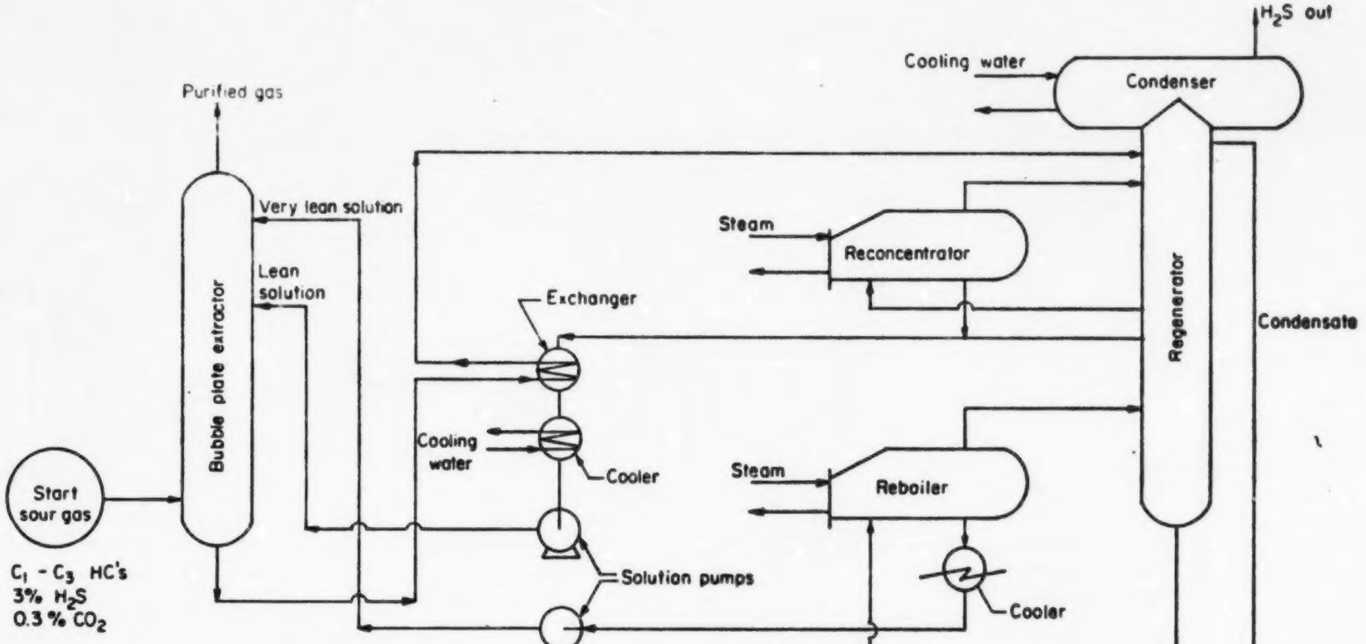

Purified gas
Scrubber tray tower
Start sour fuel gas
$C_1 - C_3$ HC's
3% H_2S
0.3% CO_2
Cooler
Amine solution
Heat exchanger
Desorption column
Steam reboiler
Steam
Condensate
Cooler
Acid gas to Claus Plant
Amine solution knock out drum
Amine solution

FIGURE A-2 FLOW DIAGRAM OF ADIP PROCESS (SHELL)


H_2S out
Cooling water
Condenser
Purified gas
Very lean solution
Lean solution
Bubble plate extractor
Steam
Reconcentrator
Regenerator
Condensate
Exchanger
Cooling water
Cooler
Steam
Reboiler
Start sour gas
$C_1 - C_3$ HC's
3% H_2S
0.3 % CO_2
Solution pumps
Cooler

Process Reaction

$K_3PO_4 + H_2S \rightleftharpoons KHS + K_2HPO_4$

FIGURE A-3. FLOW DIAGRAM FOR H_2S REMOVAL BY K_3PO_4 SOLUTION (SHELL PHOSPHATE PROCESS)

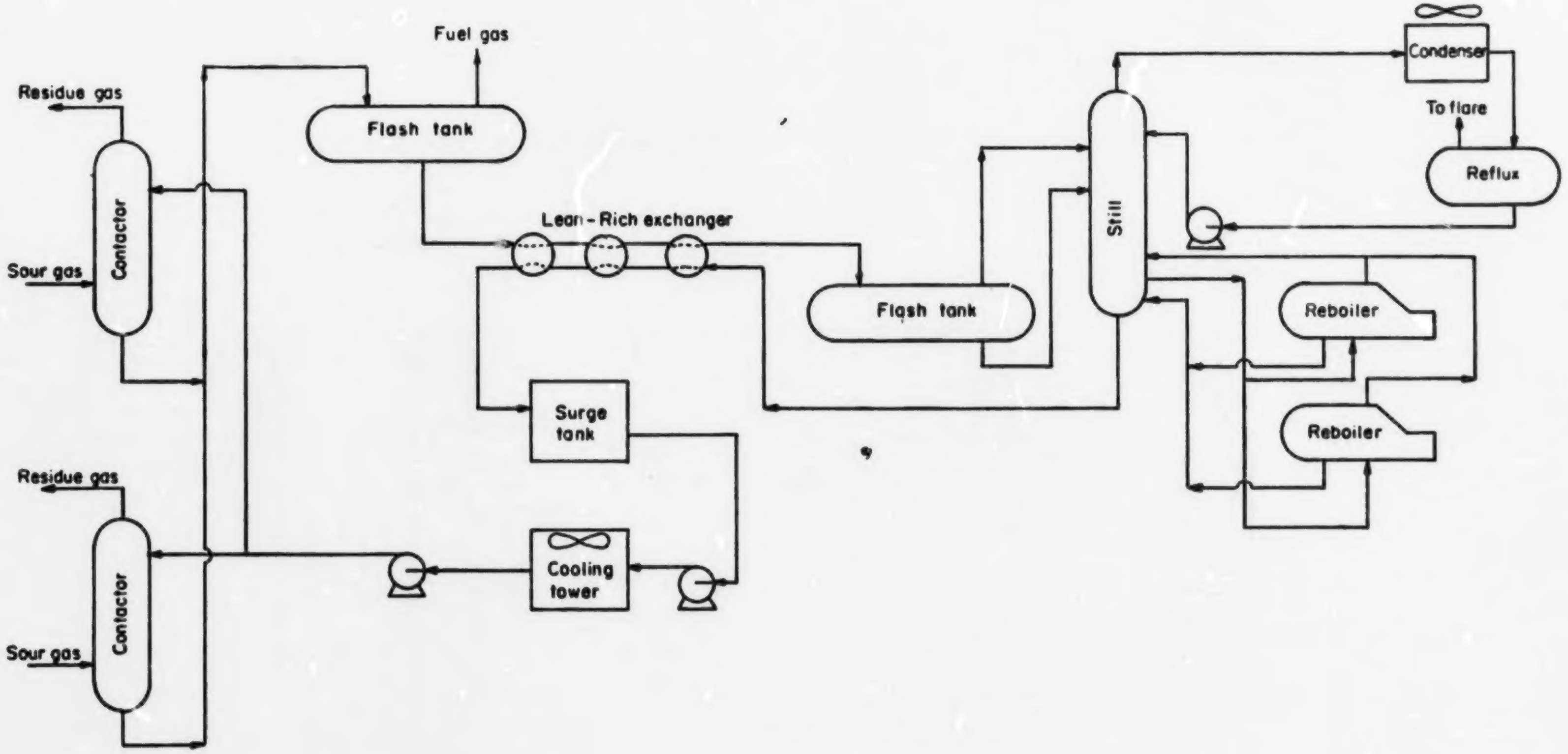

Fuel gas
Residue gas
Flash tank
Condenser
To flare
Reflux
Lean - Rich exchanger
Still
Contactor
Sour gas
Flash tank
Reboiler
Surge tank
Reboiler
Residue gas
Cooling tower
Contactor
Sour gas

FIGURE A-4. FLOW DIAGRAM OF ECONOAMINE PROCESS WITH DGA SOLUTION (FLUOR)

APPENDIX B

FLOW DIAGRAMS FOR SOUR-WATER STRIPPER

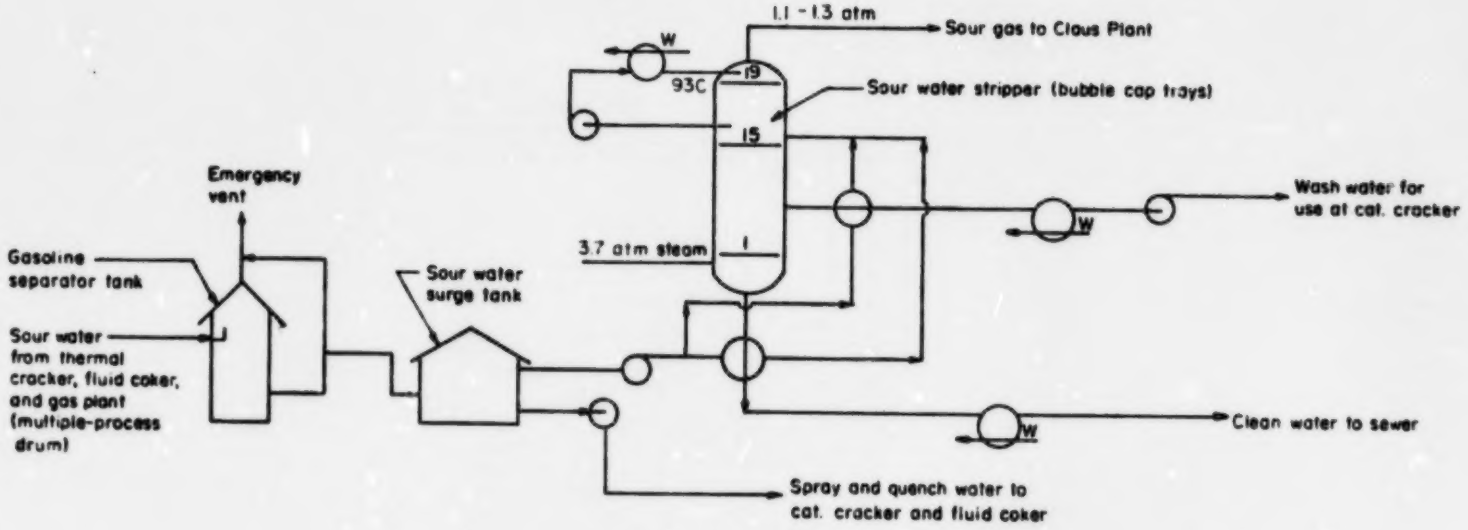

1.1 - 1.3 atm
Sour gas to Claus Plant
W
93C
19
Sour water stripper (bubble cap trays)
15
Emergency vent
3.7 atm steam
1
Wash water for use at cat. cracker
W
Gasoline separator tank
Sour water surge tank
Sour water from thermal cracker, fluid coker, and gas plant (multiple-process drum)
W
Clean water to sewer
Spray and quench water to cat. cracker and fluid coker

FIGURE B-1. REMOVAL OF SULFIDES AND AMMONIA FROM SOUR WATER BY STEAM STRIPPING

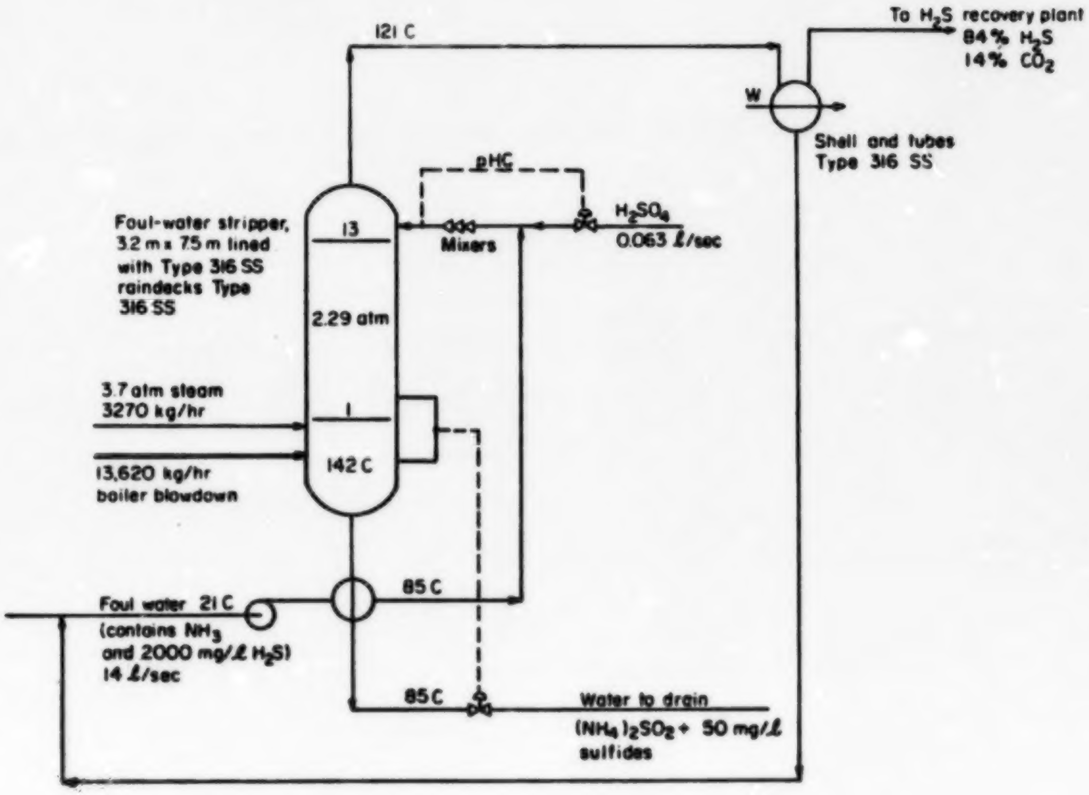

To H_2S recovery plant
84% H_2S
14% CO_2
121 C
W
Shell and tubes
Type 316 SS
pHC
H_2SO_4
0.063 ℓ/sec
Mixers
13
Foul-water stripper,
3.2 m x 7.5 m lined
with Type 316 SS
raindecks Type
316 SS
2.29 atm
3.7 atm steam
3270 kg/hr
1
142 C
13,620 kg/hr
boiler blowdown
Foul water 21 C
(contains NH_3
and 2000 mg/ℓ H_2S)
14 ℓ/sec
85 C
85 C
Water to drain
$(NH_4)_2SO_2$ + 50 mg/ℓ
sulfides

FIGURE B-2. CONTINUOUS STREAM STRIPPING OF SULFIDES FROM HIGHLY AMMONIACAL FOUL WATER

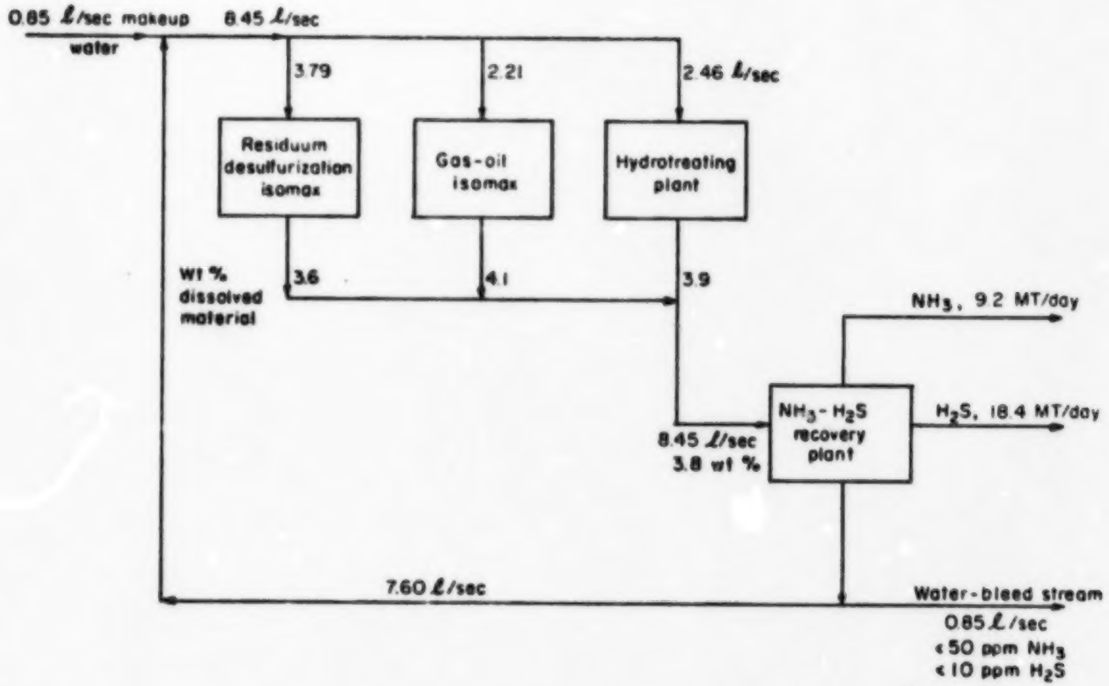

0.85 ℓ/sec makeup water
8.45 ℓ/sec
3.79
2.21
2.46 ℓ/sec
Residuum desulfurization isomax
Gas-oil isomax
Hydrotreating plant
Wt % dissolved material
3.6
4.1
3.9
NH_3, 9.2 MT/day
NH_3 - H_2S recovery plant
H_2S, 18.4 MT/day
8.45 ℓ/sec
3.8 wt %
7.60 ℓ/sec
Water-bleed stream
0.85 ℓ/sec
< 50 ppm NH_3
< 10 ppm H_2S

FIGURE B-3 SCHEMATIC BLOCK FLOW DIAGRAM SHOWING H_2S AND NH_3 BY STEAM STRIPPING

APPENDIX C

FLOW DIAGRAMS FOR RECOVERY OF SULFUR FROM ACID GASES - REFINERY CLAUS PLANTS

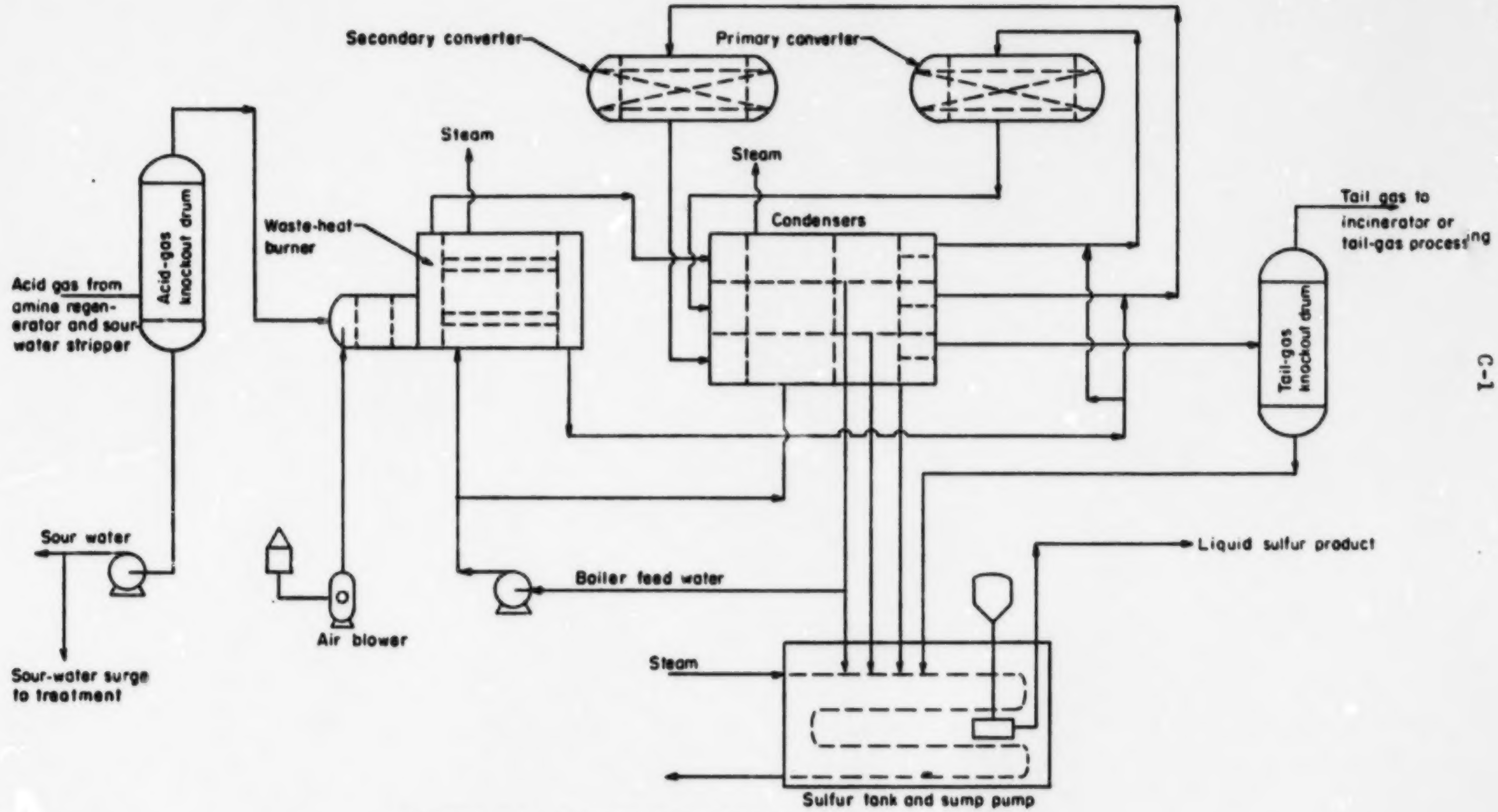

Secondary converter
Primary converter
Steam
Steam
Condensers
Waste-heat burner
Acid gas from amine regenerator and sour water stripper
Acid-gas knockout drum
Tail gas to incinerator or tail-gas processing
Tail-gas knockout drum
Sour water
Sour-water surge to treatment
Air blower
Boiler feed water
Liquid sulfur product
Steam
Sulfur tank and sump pump

FIGURE C-1. TYPICAL PACKAGED CLAUS PLANT (2 STAGE)

APPENDIX D

ALTERNATIVES TO CLAUS SULFUR PLANTS

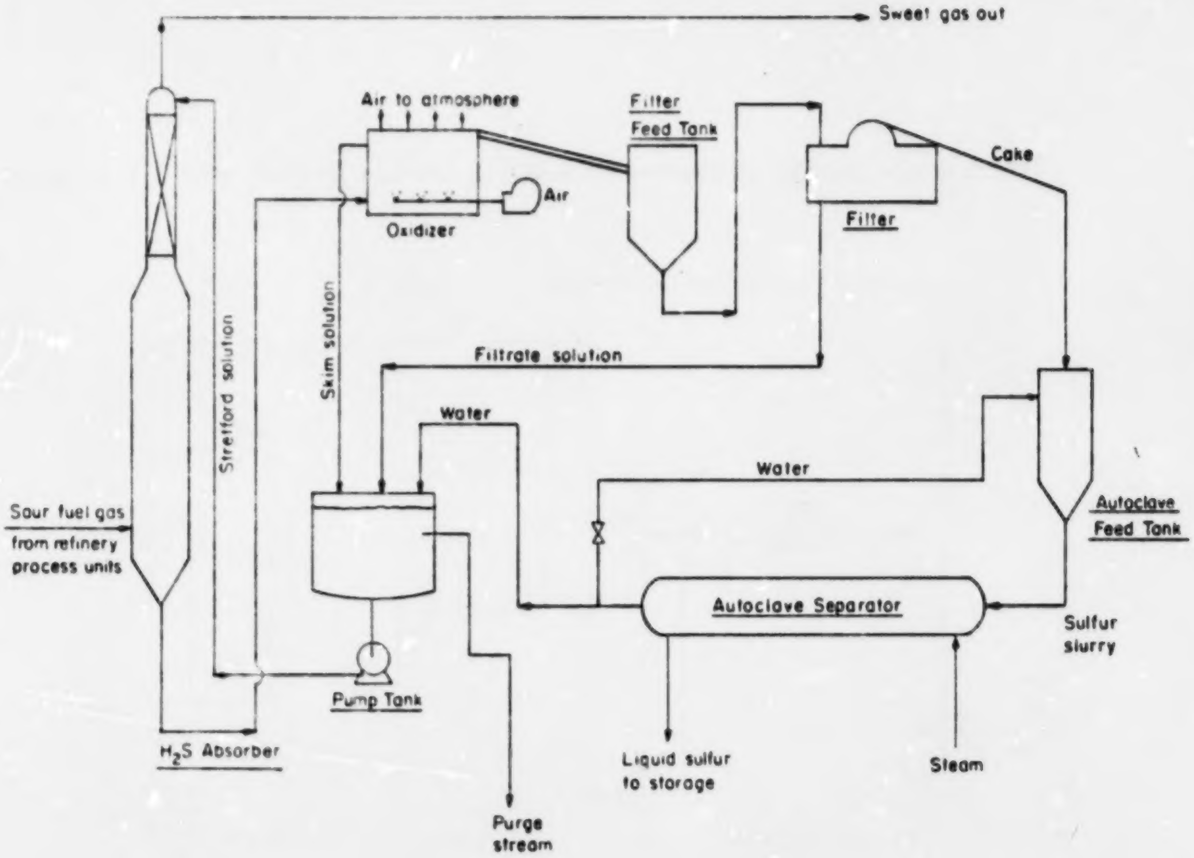

Sweet gas out
Air to atmosphere
Filter
Feed Tank
Cake
Air
Oxidizer
Filter
Stretford solution
Skim solution
Filtrate solution
Water
Water
Sour fuel gas
from refinery
process units
Autoclave
Feed Tank
Autoclave Separator
Sulfur
slurry
Pump Tank
H_2S Absorber
Liquid sulfur
to storage
Steam
Purge
stream

FIGURE D-1. STRETFORD PROCESS

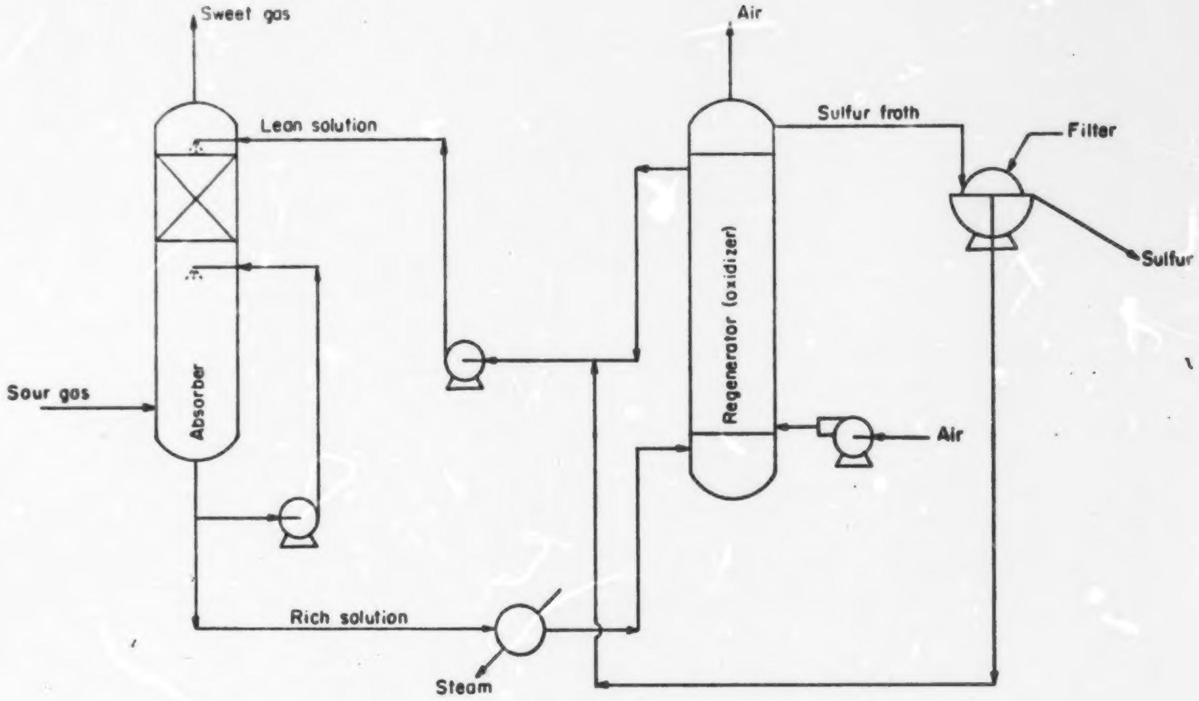

Sweet gas
Lean solution
Air
Sulfur froth
Filter
Sulfur
Sour gas
Absorber
Regenerator (oxidizer)
Air
Rich solution
Steam

FIGURE D-2. FLOW DIAGRAM FOR H_2S REMOVAL (GIAMMARCO-VETROCOKE-H_2S PROCESS)

APPENDIX E

FLOW DIAGRAMS FOR TAIL-GAS-TREATMENT PROCESSES

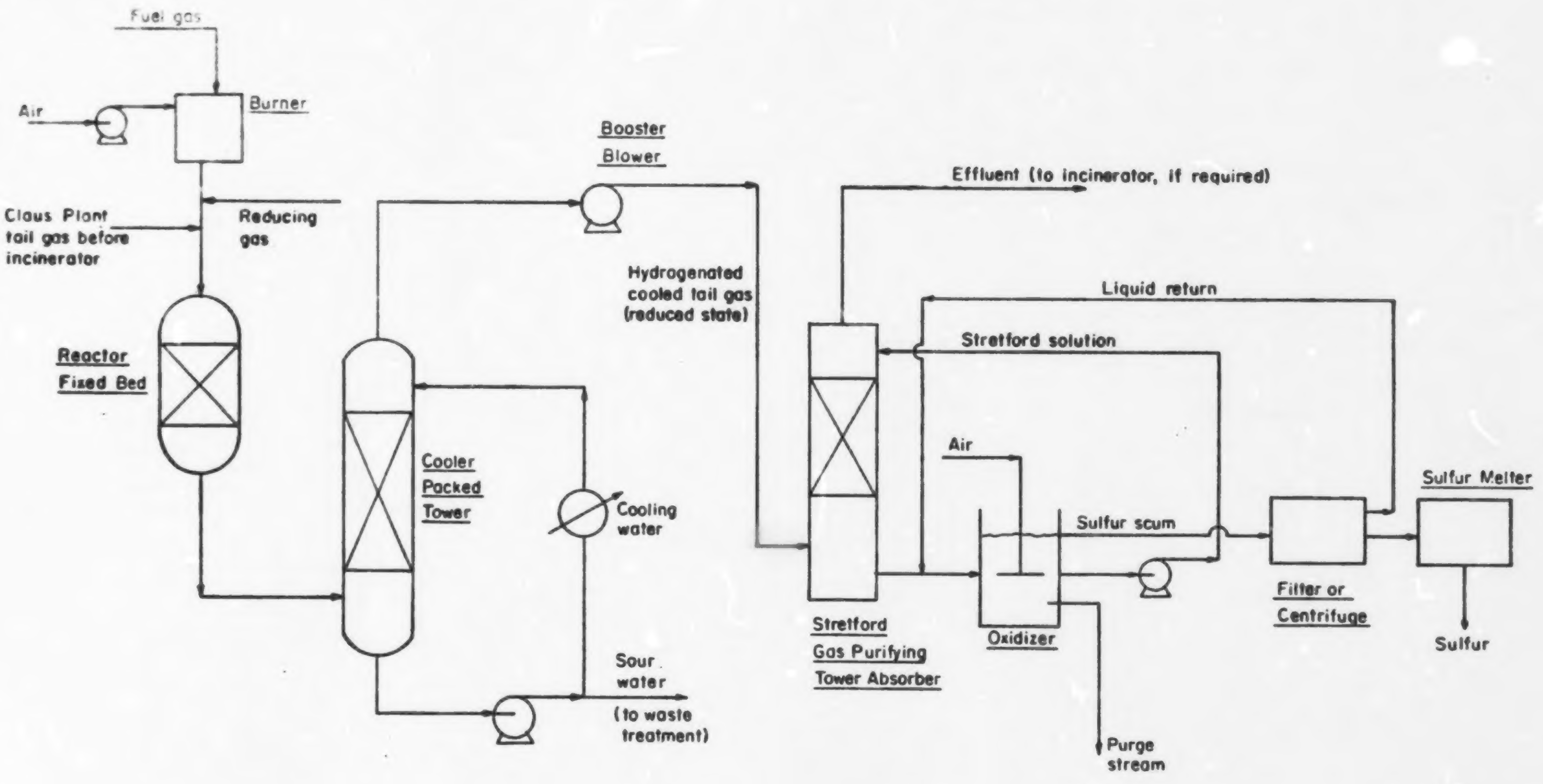

Fuel gas
Air
Burner
Claus Plant tail gas before incinerator
Reducing gas
Reactor
Fixed Bed
Cooler
Packed
Tower
Booster
Blower
Cooling water
Sour water
(to waste treatment)
Hydrogenated cooled tail gas (reduced state)
Effluent (to incinerator, if required)
Liquid return
Stretford solution
Air
Sulfur scum
Stretford
Gas Purifying
Tower Absorber
Oxidizer
Purge stream
Filter or
Centrifuge
Sulfur Melter
Sulfur

FIGURE E-1. FLOW DIAGRAM FOR THE BEAVON SULFUR-REMOVAL PROCESS

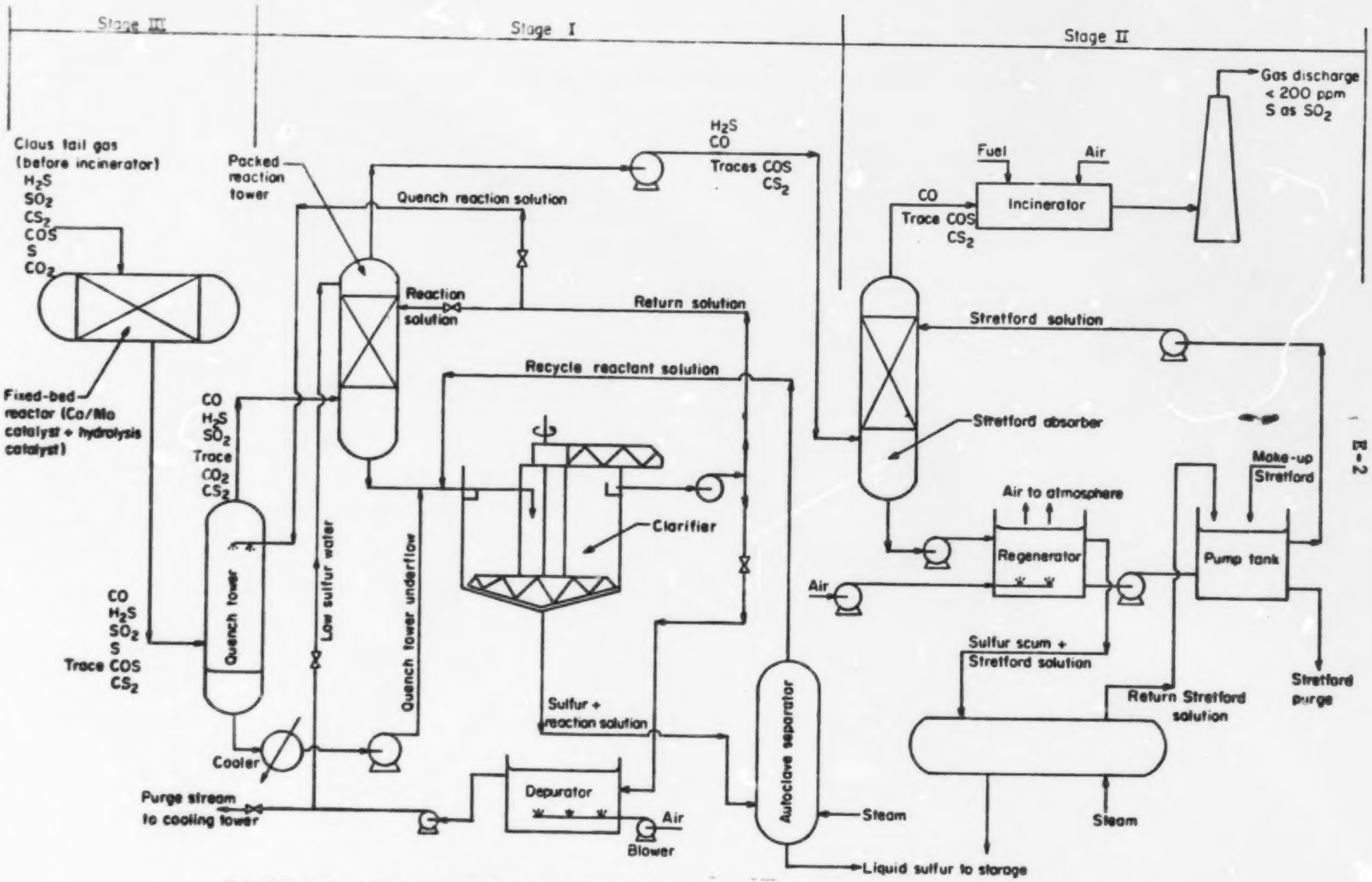

Stage III
Stage I
Stage II
Claus tail gas (before incinerator)
H_2S
SO_2
CS_2
COS
S
CO_2
Fixed-bed reactor (Co/Mo catalyst + hydrolysis catalyst)
CO
H_2S
SO_2
S
Trace COS
CS_2
CO
H_2S
SO_2
Trace
CO_2
CS_2
Quench tower
Cooler
Purge stream to cooling tower
Low sulfur water
Packed reaction tower
Quench reaction solution
Reaction solution
Quench tower underflow
H_2S
CO
Traces COS
CS_2
Return solution
Recycle reactant solution
Clarifier
Sulfur + reaction solution
Depurator
Air
Blower
Autoclave separator
Steam
Liquid sulfur to storage
CO
Trace COS
CS_2
Fuel
Air
Incinerator
Gas discharge < 200 ppm S as SO_2
Stretford solution
Stretford absorber
Air to atmosphere
Regenerator
Air
Make-up Stretford
Pump tank
Stretford purge
Sulfur scum + Stretford solution
Return Stretford solution
Steam

FIGURE E-2. SIMPLIFIED FLOW DIAGRAM FOR THE CLEANAIR CLAUS TAIL-GAS TREATMENT PROCESS

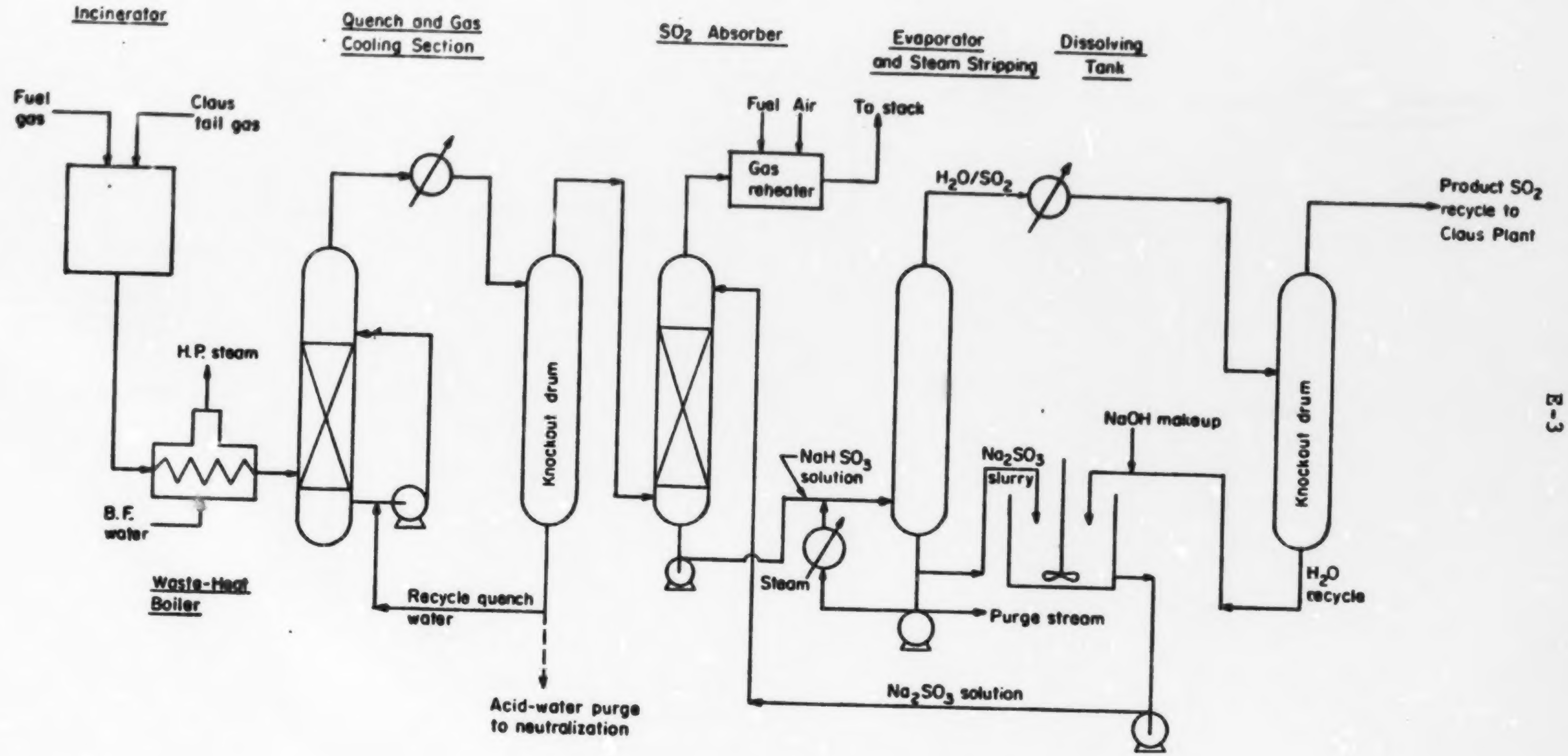

Incinerator
Quench and Gas Cooling Section
SO_2 Absorber
Evaporator and Steam Stripping
Dissolving Tank
Fuel gas
Claus tail gas
H.P. steam
B.F. water
Waste-Heat Boiler
Recycle quench water
Knockout drum
Acid-water purge to neutralization
Fuel
Air
Gas reheater
To stack
$NaHSO_3$ solution
Steam
H_2O/SO_2
Na_2SO_3 slurry
Purge stream
Na_2SO_3 solution
NaOH makeup
Knockout drum
H_2O recycle
Product SO_2 recycle to Claus Plant

FIGURE E-3 FLOW DIAGRAM FOR THE WELLMAN-LORD SO_2 RECOVERY PROCESS

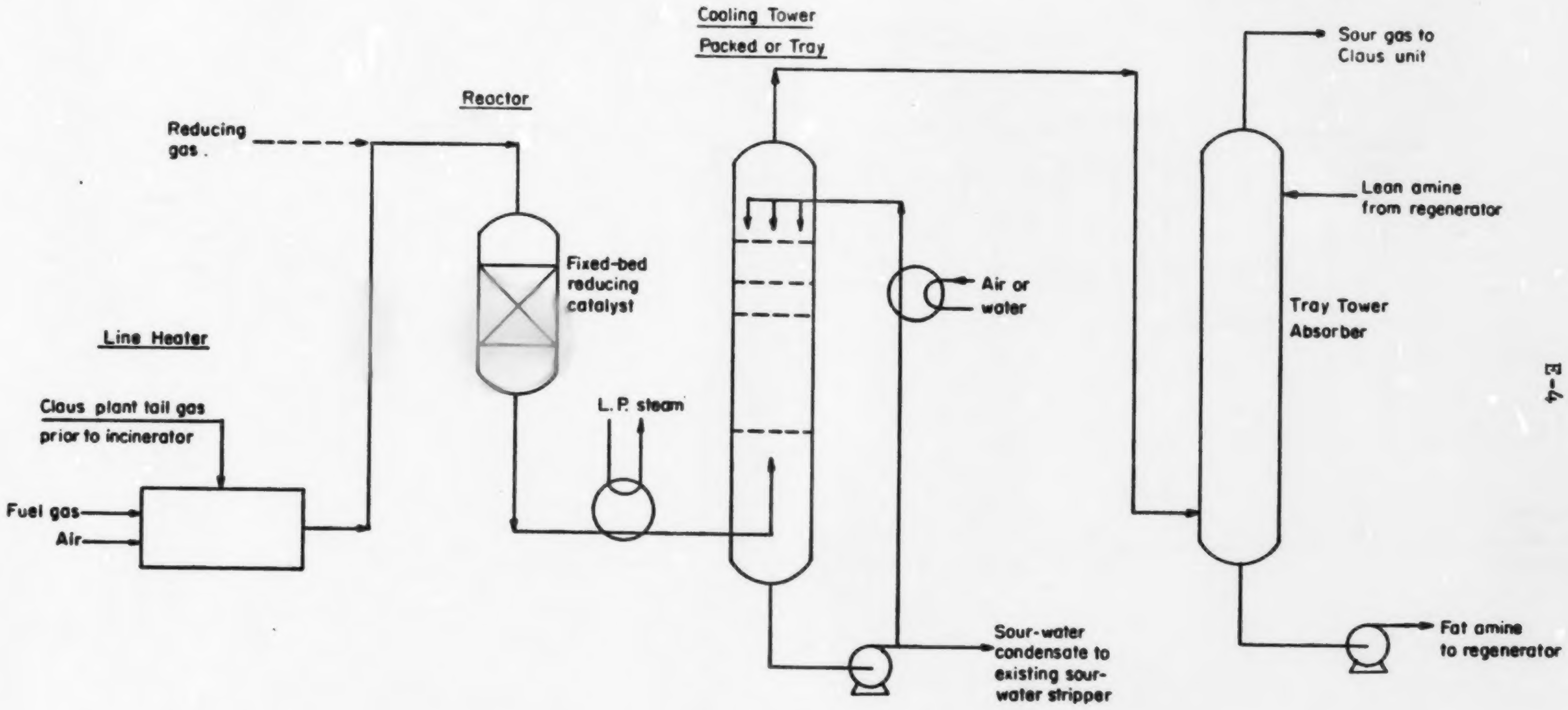

Cooling Tower
Packed or Tray
Sour gas to Claus unit
Reactor
Reducing gas .
Lean amine from regenerator
Fixed-bed reducing catalyst
Air or water
Tray Tower Absorber
Line Heater
L. P. steam
Claus plant tail gas prior to incinerator
Fuel gas
Air
Sour-water condensate to existing sour-water stripper
Fat amine to regenerator

FIGURE E4. FLOW DIAGRAM FOR THE SHELL CLAUS OFF-GAS TREATING PROCESS

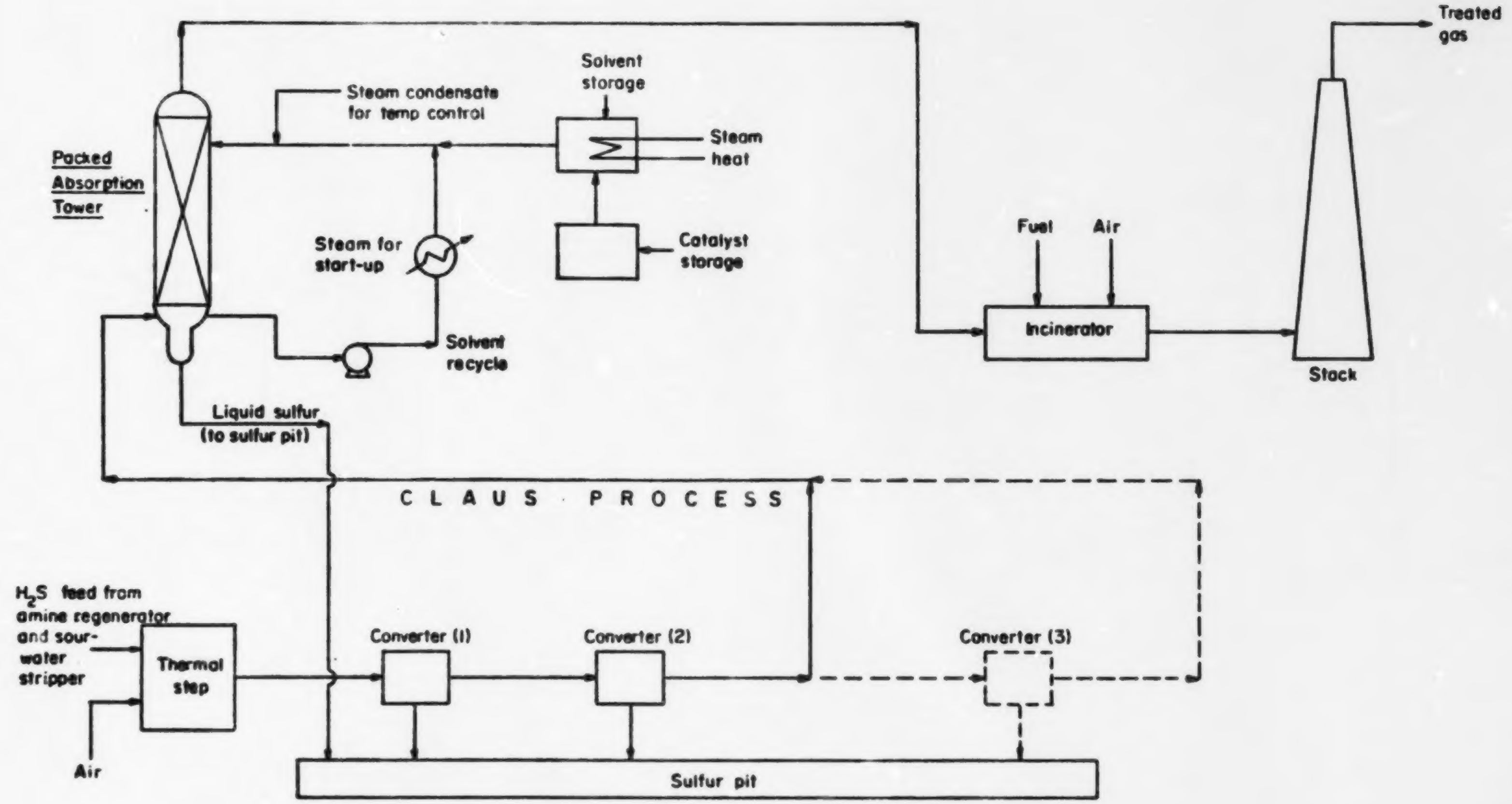

Treated gas
Stack
Incinerator
Fuel
Air
Packed Absorption Tower
Steam condensate for temp control
Solvent storage
Steam heat
Catalyst storage
Steam for start-up
Solvent recycle
Liquid sulfur (to sulfur pit)
CLAUS PROCESS
H_2S feed from amine regenerator and sour-water stripper
Air
Thermal step
Converter (1)
Converter (2)
Converter (3)
Sulfur pit

FIGURE E-5. FLOW DIAGRAM FOR IFP (TGT-1500) CLAUS TAIL-GAS CLEANUP PROCESS

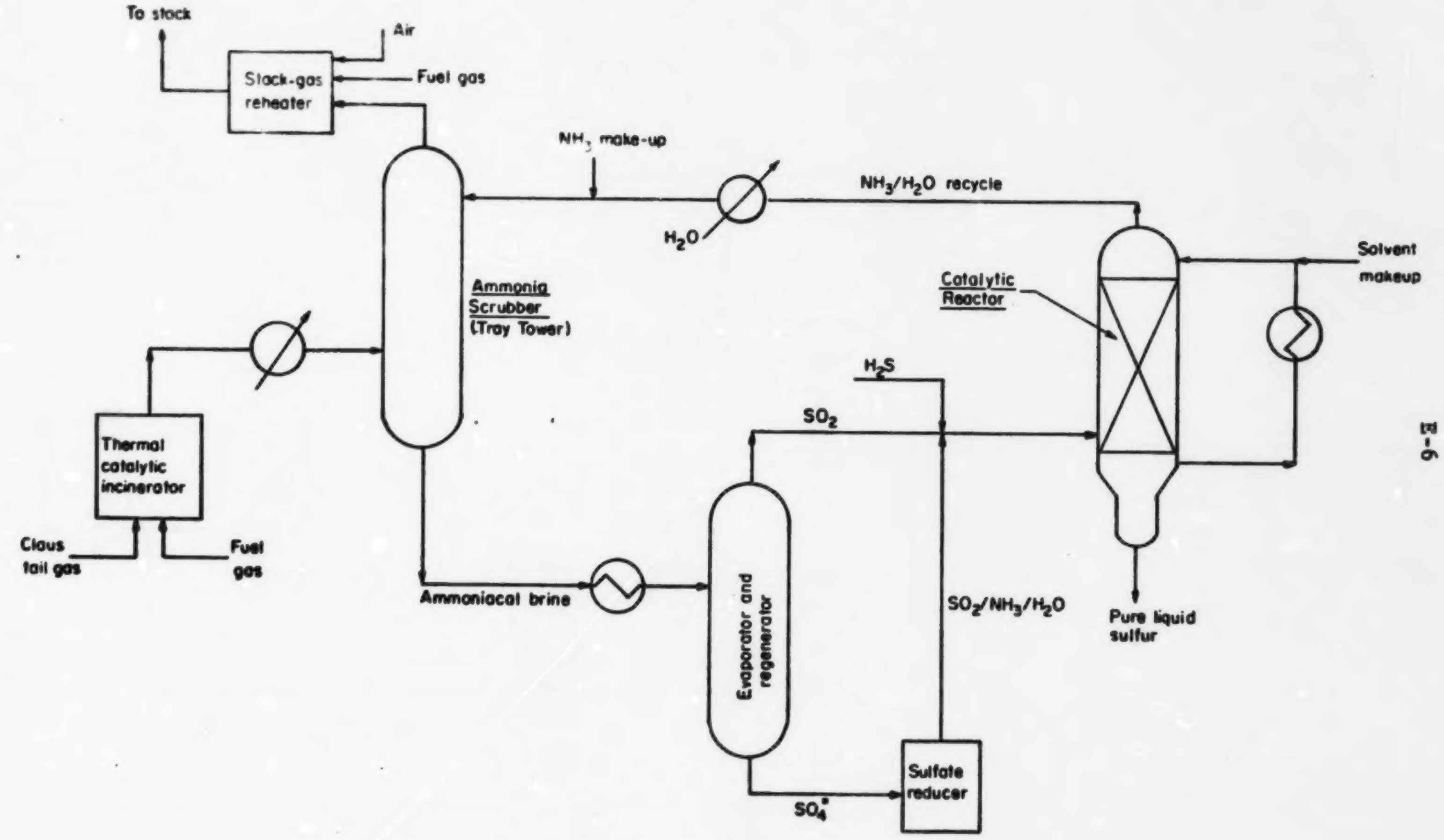

To stack
Air
Stack-gas reheater
Fuel gas
NH_3 make-up
NH_3/H_2O recycle
H_2O
Solvent makeup
Catalytic Reactor
Ammonia Scrubber (Tray Tower)
H_2S
SO_2
Thermal catalytic incinerator
Claus tail gas
Fuel gas
Ammoniacal brine
Evaporator and regenerator
$SO_2/NH_3/H_2O$
Pure liquid sulfur
Sulfate reducer
$SO_4^=$

FIGURE E-6. FLOW DIAGRAM FOR IFP (TGT-150) CLAUS TAIL-GAS CLEANUP PROCESS

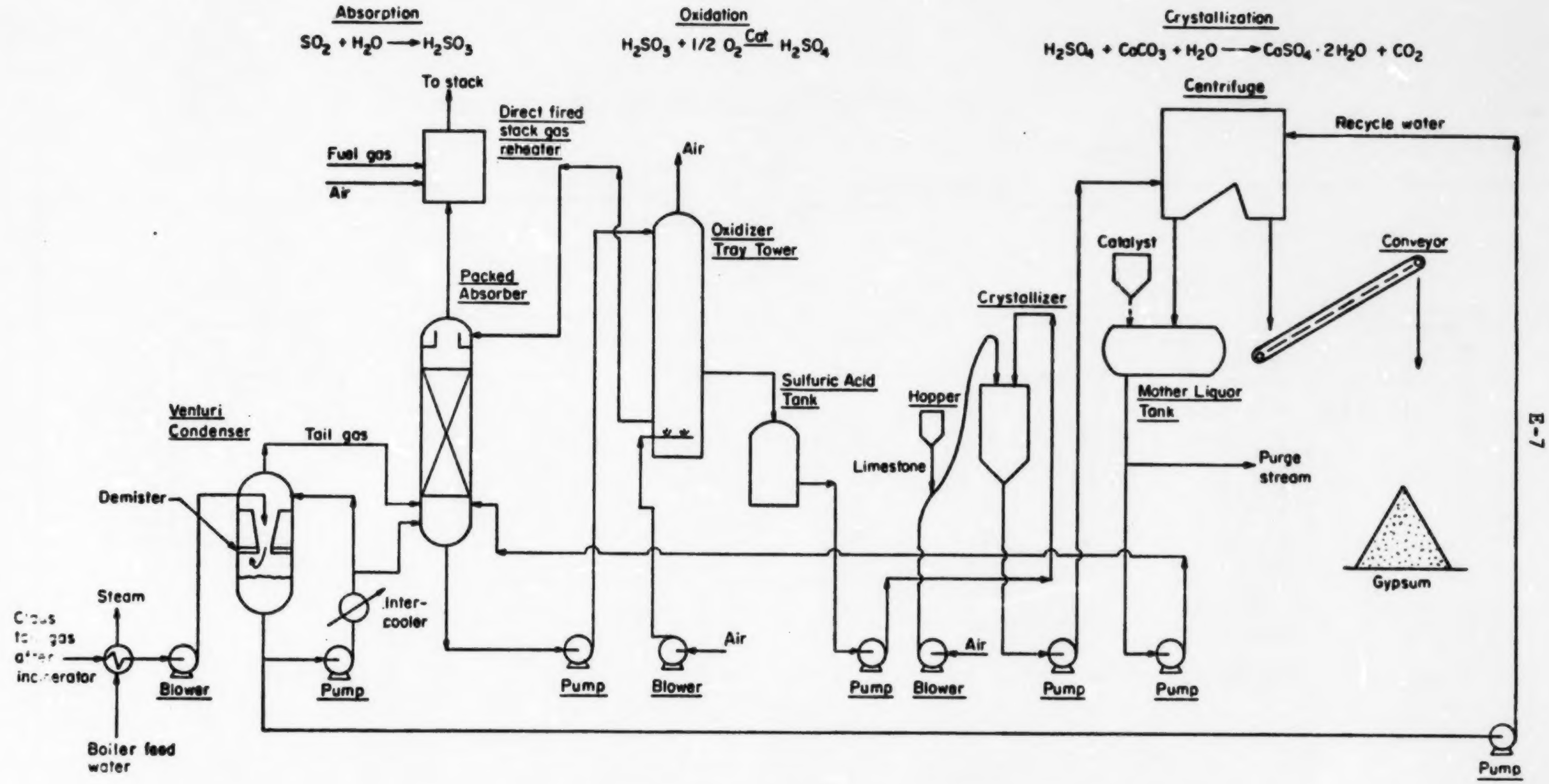

Absorption
$SO_2 + H_2O \longrightarrow H_2SO_3$
Oxidation
$H_2SO_3 + 1/2\ O_2 \xrightarrow{Cat} H_2SO_4$
Crystallization
$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2$
To stack
Direct fired stack gas reheater
Fuel gas
Air
Air
Centrifuge
Recycle water
Oxidizer Tray Tower
Catalyst
Conveyor
Packed Absorber
Crystallizer
Sulfuric Acid Tank
Hopper
Mother Liquor Tank
Venturi Condenser
Tail gas
Limestone
Purge stream
Demister
Gypsum
Steam
Claus tail gas after incinerator
Inter-cooler
Air
Air
Blower
Pump
Pump
Blower
Pump
Blower
Pump
Pump
Boiler feed water
Pump

FIGURE E-7. FLOW DIAGRAM FOR THE CHIYODA PROCESS

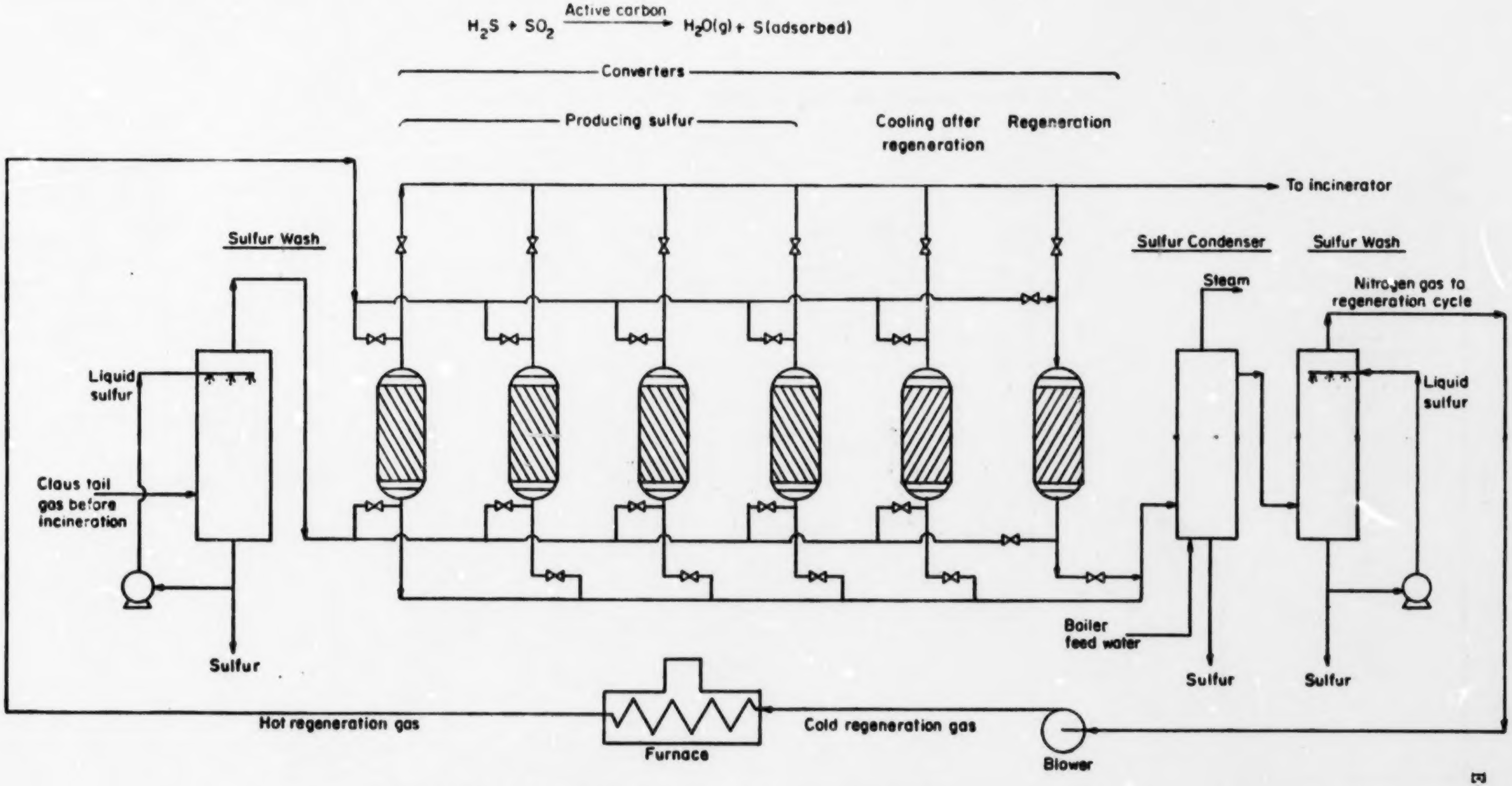

$H_2S + SO_2 \xrightarrow{\text{Active carbon}} H_2O(g) + S(\text{adsorbed})$
Converters
Producing sulfur
Cooling after regeneration
Regeneration
To incinerator
Sulfur Wash
Liquid sulfur
Claus tail gas before incineration
Sulfur
Sulfur Condenser
Steam
Boiler feed water
Sulfur
Sulfur Wash
Nitrogen gas to regeneration cycle
Liquid sulfur
Sulfur
Hot regeneration gas
Furnace
Cold regeneration gas
Blower

FIGURE E-8. FLOW DIAGRAM FOR THE SULFREEN PROCESS

APPENDIX F

PERTINENT METHODOLOGY INFORMATION

TABLE F-1. VISITS TO REFINERIES HAVING TAIL-GAS-TREATMENT EQUIPMENT

Refinery/Location/Date	Tail Gas Process	Personnel Making Visit
Standard Oil of Cal. El Segundo, Cal. October 15, 1973	Wellman-Lord	C. Sedman R. Mayfield
Douglas Oil Co. Paramount, Cal. October 16, 1973	Shell Claus Off-Gas Treating (SCOT)	C. Sedman R. Mayfield
Champlin Petrol. Co. Wilmington, Cal. October 18, 1973	SCOT	J. Genco C. Sedman
Gulf Oil Co. Philadelphia, Pa. October 10, 1973	Cleanair	C. Sedman J. Durham D. Marsland
Gulf Oil Co. Sante Fe Springs, Cal. October 16, 1973	Cleanair	C. Sedman R. Mayfield
Atlantic Richfield Co. Carson, Cal. October 17, 1973	Cleanair	J. Genco C. Sedman R. Mayfield
Mobile Oil Co. Torrance, Cal. October 18, 1973	Beavon	J. Genco C. Sedman
Union Oil Co. Wilmington, Cal. October 19, 1973	Beavon	J. Genco C. Sedman

TABLE F-2. LIST OF SULFUR TAIL GAS PROCESS VENDORS

Process	Vendor	Contact	Telephone
Wellman-Lord	Davy Power Gas Co. P.O. Box 2436 4715 S. Florida Ave. Lakeland, Florida 33803	Gerald J. Smith, President	(813) 646-7100
Beavon process (Stretford)	Union Oil of California Research Department P.O. Box 76 Brea, California	A. S. Kasperik, Consultant to Technology Sales	(714) 528-7201
	Ralph M. Parsons Company P.O. Box 54802 617 W. Seventh St. Los Angeles, Cal. 90054	cc: O. G. Roddey, Vice President Precontract and Process	
Cleanair	J. F. Pritchard & Company 4625 Roanoke Parkway Kansas City, Missouri 64112	J. Peter Richardson cc: Andrew J. Robell, Manager, Licensing & Patents	(816) 531-9500
SCOT	Shell Development Company P.O. Box 100 Deer Park, Texas 77536	Dr. C. L. Oubre Manager, Pet. Processes and Engineering R. Manning, Senior Engineer	(713) 479-2311

TABLE F-2. (Continued)

Process	Vendor	Contact	Telephone
IFP	Institut Francais du Petrole 90 Park Avenue New York, N.Y. 10016	J. W. Andrews	(212) 751-8335
Chiyoda	Chiyoda Chemical Eng. & Construction Co., Ltd. P.O. Box 10 Tsurumi, Yokohama Japan	M. Sato, Executive Managing Director	Telex: Chiyo J47726
Cataban	Rhodia, Incorporated 600 Madison Avenue New York, N.Y.	W. C. Meuly	(212) 753-4850
Sulfreen	Societe Nationale des Petroles d'Aquitaine 92 Courbevoie France	G. L. Guyot	Telex: Petrak 62952

November 30, 1973

Mr. Gerald J. Smith, President
Davy Power Gas Company
P. O. Box 2436
4715 South Florida Avenue
Lakeland, Florida 33803

Treatment of Claus Plant Tail-Gas Streams in Refinery Operations Using the Wellman-Lord Process

Dear Mr. Smith:

The Environmental Protection Agency, Office of Air Programs, has engaged Battelle-Columbus Laboratories to perform a technical review of processes available for the recovery of sulfur from Claus Plant tail-gas streams in petroleum refineries (Contract 68-02-0611). This program is being conducted to provide EPA with technical information for setting possible sulfur-emission regulations from refinery-operated Claus plants.

I understand that the Davy Power Gas Company is a leading process engineering firm in the petroleum and petrochemical industry and the developer of the Wellman-Lord tail-gas process. It would be most helpful to this study if you would provide the following technical information concerning the Wellman-Lord process:

(1) Process users - A list of the refineries, both foreign and domestic, that are now using or plan to use the Wellman-Lord tail-gas treating process. Please give the location, size of the Claus sulfur plant being served, and the approximate removal efficiency or ppm level being achieved with the exhaust-gas stream from the tail-gas unit (prior to incineration).

(2) Process basis - A process-flow diagram and a description of the technical basis for its operation.

(3) Material and energy balances - For a 100 LT/D Claus sulfur plant having a tail gas with the

properties shown in Table 1, can you provide approximate material- and energy-balance information if the tail gas were to be treated with the Wellman-Lord process?

(4) Process efficiency - In general, what is the lowest practical outlet-sulfur concentration attainable with the Wellman-Lord process (prior to incineration), and what variables does this depend on?

(5) Trace materials - How are impurities such as COS, CS_2, and entrained sulfur (vapor and mist) handled?

(6) Process requirements - What are the approximate utilities, i.e., fuel gas, electric power, chemicals, steam, and cooling water and manpower requirements for treating the tail gases from 100 and 1,000 MT/D Claus plants? (Use Table 1 as a basis if need be.)

(7) Chemicals and catalysts - Are there any special chemicals and catalysts required in the Wellman-Lord process?

(8) Process changes - What is the effect of varying the sulfur content of the crude, and of increases and decreases in crude through-put?

(9) Process waste streams - Are there any process-waste streams generated in your tail-gas process?

(10) For a 100 MT/D Claus sulfur plant (see Table1), how large are the waste streams, what is their approximate composition, and how are they treated and/or disposed of?

I would appreciate greatly receiving the above information as soon as possible. For those questions and areas that may involve proprietary information, please indicate it in your reply. In this case, Battelle would be happy to sign a secrecy agreement with your company if you so desire. After receiving the above information, it is likely that I will want to talk either to you or one of your colleagues to clarify my understanding of your process. Further, if possible I would like to arrange a visit or perhaps talk to a technical representative from your company.

TABLE 1. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING HYPOTHETICAL 100 MT/D REFINERY CLAUS PLANT (Basis: sulfur recovery in Claus unit of 94 percent)

Composition		Claus Intake	Claus Tail Gas	
			Before Incineration	After Incineration*
H_2S	, % vol.	89.9	0.85	--
SO_2	, "	--	0.42	1.08
S_8 vapor and mist,	"	--	0.05	--
COS	, "	--	0.05	--
CS_2	, "	--	0.04	--
CO	, "	--	0.22	--
CO_2	, "	4.6	2.37	4.23
(MW:30)	, "	0.5	--	--
H_2	, "	--	1.60	--
H_2O	, "	5.0	33.10	26.57
N_2	, "	--	61.30	66.68
O_2	, "	--	--	1.44
Total		100.0	100.00	100.00
Temperature, C		40	140	650
Pressure, atm		1.45	1.26	1.00
Gas quantity, mole Relative amount		1	3.0	5.01
Flow, scmm		56.78	170.35	284.48

* Based on using 10 percent excess air in the incinerator and CH_4 as fuel.

Your kind assistance in this matter is greatly appreciated.

Sincerely yours,

Joseph M. Genco
Senior Engineer
Emissions Control and Environmental
Systems Division

JMG:clb

cc: Mr. Charles B. Sedman, Engineer
Industrial Studies Branch
Environmental Protection Agency
Durham, North Carolina 227711

Mr. James Durham, Section Chief
Industrial Studies Branch
Environmental Protection Agency
Durham, North Carolina 27711